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LEAD SILICATES

II. OPTICAL AND THERMAL ANALYSIS OF THE SYSTEM PbO-SiO_2

By H. C. COOPER, E. H. KRAUS AND A. A. KLEIN

The present article gives new observations in the thermal and optical analysis of the lead oxide–silica series and treats of the relation to the series of the two simple lead silicate minerals, barysilite, $3PbO : 2SiO_2$, and alamosite, $PbO : SiO_2$, and the lead silicate crystals found under lead furnaces. The article results from (1) a continuation by H. C. Cooper (Syracuse University) of the thermal analysis of the lead oxide–silica system begun in 1907 by Cooper, Shaw and Loomis,[1] (2) a microscopic investigation of natural and artificial preparations by E. H. Kraus and A. A. Klein (University of Michigan), and (3) a collaborative microscopic and interpretative study at Ann Arbor by H. C. Cooper and E. H. Kraus.

The earlier work of Cooper, Shaw and Loomis consisted in the preparation and crystallization (from the melt) of a large number of lead silicate mixtures, the determination of heating curves, development of the melting-point curve, and the thermal-analytical conclusion that the orthosilicate Pb_2SiO_4 and the metasilicate $PbSiO_3$ are well-defined compounds. At the same time Hilpert and Weiller were making an in-

[1] THIS JOURNAL, 42, 461. Ber. d. chem. Ges., 42, 3991.

dependent study of this system at Berlin and their account[1] antedates that of Cooper, Shaw and Loomis by a few weeks. The curious results of Hilpert and Weiller were subjected to an early revision by Hilpert and Nacken[2] after the work of Cooper, Shaw and Loomis appeared and the final conclusions were as follows: The study of cooling curves gave no very satisfactory results, but with the aid of Dr. Nacken's stirring device[3] indications were observed pointing to the existence of the compounds Pb_2SiO_4 and $PbSiO_3$ and the possible existence of the 3 : 1 and 3 : 2 compounds. Necessarily rough measurements of crystallization velocity and spontaneous crystallizing power (Tammann's *KG* and *KV*) gave results that could be harmonized with the above conclusions. The optical properties of the 3 : 2 preparation also indicated that a new individual was involved. The density (specific volume) curve was not very instructive.

In continuing our work we have taken into consideration (1) the mineral *barysilite*, specimens of which from the Harstig (original material) and Längban mines had been kindly placed at our disposal by Intendant Sjögren of the Royal Museum of Natural History, Stockholm; (2) the new mineral *alamosite*,[4] analyzing as the metasilicate, fragments of which were loaned by Professor C. Palache of Harvard University, one of the discoverers; (3) specimens of possible lead silicates found under dismantled lead furnaces and generously supplied by Mr. F. P. Graves of Doe Run, Missouri; and (4) numerous crucible preparations of various mixtures of lead oxide and silica, prepared by slow cooling of the melt.

Of the several methods of study, the microscopic work has been most fruitful. The optical identification of the lead silicates is, however, uncommonly difficult, because the refractive indices of lead oxide and lead silicate compounds are very high, being approximately 2. Since we have no liquid with an index as high as 2, the valuable Schroeder van der Kolk method of determining the refractive indices of grains by

[1] Ber. d. chem. Ges., **43**, 2969.
[2] *Ibid.*, **43**, 2565.
[3] Centralb. f. M., G. und P., **1910**, 454.
[4] Am. J. Sci., **27**, 399 (1909).

immersion is not available and the utilization of liquid immersion for detecting heterogeneity is impossible. The optical study resolves itself, therefore, into a painstaking survey of the powdered material under the microscope with reference to structure, cleavage, color and optical character.

The optical work dealt with the following: specimens of barysilite and alamosite, crystal specimens found under a lead smelter and a series of crucible preparations in the lead oxide–silica series, all made by slow cooling of the melt; and, finally, with lead oxide and silica as end members of the series. The observations were made on thin sections and fragments, immersed in methylene iodide ($n = 1.74$). The indices of refraction were studied by observing the relief with the condensing system at various levels, also by the Becke and Schroeder van der Kolk methods. In all cases the double refraction was ascertained roughly from the interference colors.

1. *Preparations Involving Lead Metasilicate.*—These consisted of the alamosite fragments and cooled melts of mixtures containing from 48–52 per cent. lead oxide.

a. Alamosite (type material) from Alamos, Sonora, Mexico: The fragments were colorless and showed good cleavage in one direction. Inclined extinction was observed. The indices of refraction and the double refraction were high. The interference figure was biaxial with a positive double refraction. This is in harmony with the geometrical form of the crystals, which were shown by Palache's measurements to be monoclinic.

b. Thin section and fragments of melt containing 50 equivalent–per cent. lead oxide ($1PbO : 1SiO_2$): This was homogeneous throughout. The texture was rather granular with a cleavage in one direction. Inclined extinction was observed. The indices of refraction, as well as the double refraction, were very high. The substance showed a positive biaxial interference figure.

c. Thin section of melt containing 48 equivalent–per cent. lead oxide: This is a more siliceous composition than the 1 : 1 mixture. The section consisted mainly of a colorless substance. The texture was more or less granular and a cleavage was ob-

served in one or two directions. The extinction was inclined and the interference figure biaxial positive. This substance corresponds to that of the 1 : 1 preparation. The indices of refraction and the double refraction were very high. Throughout the section quartz was scattered, sometimes in irregular grains, but also in well-defined crystals of hexagonal outline. These were distinguished by the characteristic low indices of refraction, low birefringence and positive uniaxial interference figure. Considerable glass was present.

d. Thin section of melt containing 42.9 equivalent – per cent. lead oxide ($3PbO : 4SiO_2$), a still more siliceous composition: The optical characteristics were the same as for the 48 per cent. melt, except that the crystals were smaller and the proportion of glass larger.

e. Crystal fragments and thin section of melt containing 52 equivalent – per cent. lead oxide, a mixture containing more lead than the 1 : 1 melt: The fragments showed two substances. The predominating one was biaxial positive with a moderately high double refraction. Cleavage was observed in one direction and the extinction was inclined to it. The double refraction was high. This substance, again, corresponds to that of the 1 : 1 melt. The other substance showed high index with a positive biaxial interference figure. It was slightly pleochroic and somewhat resembled lead oxide. In specimens cooled slowly without long baking, or "sintering," a large proportion of the melt remained vitreous.

Conclusion.—The above optical observations indicate that the artificial melt containing 50 equivalent – per cent. lead oxide ($1PbO : 1SiO_2$) is a definite compound, namely, the metasilicate, $PbSiO_3$, and that it is identical with the mineral alamosite optically, as well as physically. It is interesting that the mineral was prepared in the laboratory before it was found in nature.

2. Preparations Involving Lead "Pyrosilicate," $Pb_2Si_2O_7$, Occurring as the Mineral Barysilite.—There were various specimens of barysilite and crystal fragments and thin sections of the melt containing 60 equivalent – per cent. lead oxide

($3PbO : 2SiO_2$), besides melts of adjacent compositions; also preparations of a probable lead silicate from a smelter.

a. Fragments and thin section of the original barysilite material from the Harstig mine, Pajsberg, Sweden: The mineral was homogeneous, being colorless and showing a columnar structure with cleavage cracks perpendicular to the length of the fibers. The indices of refraction were probably over two; the mineral was uniaxial with a negative double refraction. The double refraction was not very strong.

b. Lamellae of barysilite from the Längban mine, Sweden: It should be noted that the superficial layer of the Längban specimens is a mixture. The hard white material with a pearly luster is not lead silicate. The real barysilite is lamellar and of a vitreous luster, resembling mica and has a medium double refraction. These lamellae in a thickness of 0.01–0.02 mm. show a splendid uniaxial figure of a negative character.

c. Crystal fragments and a thin section of the melt containing 60 equivalent-per cent. lead oxide ($3PbO : 2SiO_2$): These were colorless and appeared to be homogeneous throughout. The structure was similar to that of the barysilite from the Harstig mine with the cleavage cracks running across the fibers. The indices of refraction were very high. The substance showed a negative uniaxial interference figure. The double refraction also appeared to be high. In one preparation some biaxial positive material (metasilicate?) was observed. On the whole, however, the preparation was essentially homogeneous and the resemblance of the natural and artificial material is quite convincing.

d. Fragments of the melts containing 59, 58 and 57 equivalent-per cent. lead oxide, more siliceous than the 3 : 2 mixture: These melts were cooled very slowly through the significant range of temperature. In the order given they showed an increasing proportion of biaxial positive material of parallel extinction. The 59 per cent. melt alone showed the columnar uniaxial negative material of the 60 per cent. preparation (3 : 2). The structure was mostly finely granular and even mossy—rather characteristically eutectic. The 58 per cent. mixture, prepared, as stated, by retarded cooling, exhibited a very slight tendency

to crystallize and most of the crystalline material was very finely granular. The 57 per cent. preparation crystallized a little better under the same conditions. The granular structure was coarser than in the 58 and 59 per cent. melts. The structure and low crystallizing power suggest a eutectic point at 58 per cent.

e. Crystal fragments of the melts containing 61 and 62 equivalent – per cent. (prepared by slow cooling): Their structure was fibrous to columnar, with cross cleavage. The crystals characteristic of the 60 per cent. preparation appeared in decreasing amount. In the 62 per cent. preparation there appeared a little of the biaxial negative substance characteristic of the 2 : 1 mixture (orthosilicate, see below). There was also considerable biaxial positive substance, as in the lower percentage preparations. Unfortunately there appeared to be no means of identifying this substance. In none of the preparations between the 3 : 2 and 2 : 1 compositions was there any optical evidence of a eutectic mixture.

f. Crystals and thin section of lead silicate from a smelter: It is appropriate to append here a report on the smelter silicate. The specimen observed was found under the hearth of an old lead furnace at Doe Run, Missouri. It was supposed to be artificial barysilite. It corresponds rather closely to the specimens of similar origin, described by Dana and Penfield[1] and Wheeler[2] and found to have a composition expressed by the ratio $7PbO:4SiO_2$. As the observations on the present specimen supplement those of the scientists mentioned, these are given in full.

Crystallography.—The crystals were prismatic in development (see Fig. I), of a brownish color and of a luster which was more or less vitreous. They were imbedded in a matrix which was granular in structure and had a resinous luster, resembling that of sphalerite.

The forms observed were $c(0001)$, $p(10\bar{1}1)$, $m(10\bar{1}0)$ and $a(11\bar{2}0)$. The predominating forms were (0001) and $(10\bar{1}0)$, the other forms, $(10\bar{1}1)$ and $(11\bar{2}0)$, being small. Excellent

[1] Am. J. Sci., [3] **30**, 138 (1885). Z. Kryst., **11**, 310.
[2] Am. J. Sci., [3] **32**, 272 (1886).

reflections of the signal were obtained on (0001), fairly good on $(10\bar{1}0)$, whereas on $(10\bar{1}1)$ and $(11\bar{2}0)$ shimmer readings had to be resorted to and the average of several readings

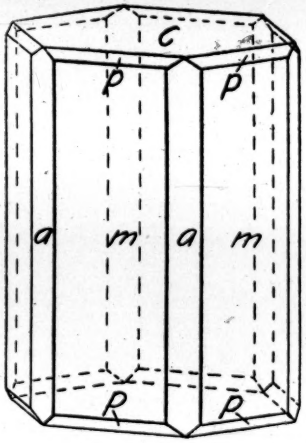

Fig. 1

taken. Of these forms $(11\bar{2}0)$ was not observed by Dana and Penfield, who give the value $c : p$ roughly as about 50°.

The readings gave:

Class of crystallization: dihexagonal bipyramidal; axial ratio: $a : c = 1 : 1.0246$. Dana and Penfield gave $a : c = 1 : 1.032$ on account of the difference in the reading of $c : p$.

	Observed	Average	Calculated
$c : p = (0001)\ (10\bar{1}1)$	$= 49° 41' 36''$	24 readings	...
$c : m = (0001)\ (10\bar{1}0)$	$= 89° 58'$	5 "	90°
$m : m = (10\bar{1}0)\ (01\bar{1}0)$	$= 59° 59'$	4 "	60°
$m : a = (10\bar{1}0)\ (11\bar{2}0)$	$= 29° 55'$	10 "	30°

Physical and Optical Properties.—Cleavage fragments were found to have a conchoidal fracture with indications of a cleavage parallel to (0001). The thicker sections were pleochroic, showing deep orange to light yellow with the ordinary ray

(a) corresponding to the orange. Very thin sections were colorless. The indices of refraction, as well as the double refraction, were high. The interference figure was positive uniaxial. The thin section was not homogeneous. It consisted of a substance having the above properties, except that it showed a positive uniaxial interference figure. Intimately associated with it was another substance having the above properties but showing a negative uniaxial interference figure. Magnetite crystals were scattered throughout the slide and a perfect crystal of augite was noted.

Conclusion.—From the optical analysis we conclude that the mixture with 60 equivalent-per cent. lead oxide represents a definite compound, $Pb_3Si_2O_7$ ($3PbO : 2SiO_2$), lead "pyrosilicate," optically negative in character, and that it occurs in nature as the mineral barysilite, bearing also, however, various added mineral substances in solid solution; further, that the structure and crystallizing tendency point to a eutectic mixture at or near the composition 58 equivalent-per cent. lead oxide. The so-called "lead silicate" found under lead smelters is of indefinite composition, being probably a complex solid solution of lead and other silicates. Its optical properties are so hard to characterize—probably because the variable admixtures make variable properties—that little can be done toward defining the compound involved. Furthermore, one may well question whether the task is worth attempting with our present means.

3. Preparations Involving Lead Orthosilicate (all Artificial)

a. Crystal fragments and thin section of the melt containing $66^2/_3$ equivalent-per cent. lead oxide ($2PbO : 1SiO_2$). These were colorless and appeared to be homogeneous. They were fibrous or columnar in structure and much cross-cleaved. They showed parallel extinction and gave a negative biaxial interference figure. The indices of refraction were high, as also the double refraction. The statement in the article of Cooper, Shaw and Loomis,[1] that it is hexagonal was based on incomplete observation.

[1] P. 473.

b. Crystal fragments and thin section of melt containing 65 equivalent–per cent. lead oxide. The structure was mostly columnar and resembled the 2 : 1 structure. The preparation examined in the form of fine powder consisted about half of a substance, white or pale yellow under crossed nicols, giving a uniaxial negative interference figure. The substance resembled barysilite. The other half of the preparation consisted of material which was highly colored under crossed nicols and gave a biaxial interference figure, but the optical character of some grains was negative, as for the 2 : 1 mixture, and that of others was positive and their identification was not possible.

c. Thin section of the melt with 69 equivalent–per cent. lead oxide, a mixture containing more lead oxide than the orthosilicate. The section was not homogeneous. One of the constituents was a colorless substance with fibrous structure showing cross-cleavage. Parallel extinction was observed. The indices of refraction and the double refraction were both high. The interference figure was negative biaxial. These properties correspond to those of the 2 : 1 melt. Throughout the slide was observed a brown and rather opaque substance showing anomalities both in the interference color and in the interference figure. The interference color was a characteristic anomalous blue and the figure showed an anomalous curved cross, which was not altered in monochromatic light.

These anomalities have yet to be fully investigated. They are also observed in some of the preparations of mixtures richer in lead oxide.

Conclusion.—According to the optical analysis the melt containing $66^2/_3$ equivalent–per cent. lead oxide (2 : 1) appears to be a definite compound of the formula Pb_2SiO_4, the orthosilicate. It is negative biaxial. It has not yet been found in nature.

4. Preparations with upwards of 70 Equivalent–Per Cent. Lead Oxide

a. Crystal fragments of the melt containing 75 equivalent–per cent, lead oxide ($3PbO : 1SiO_2$): The texture was columnar with

strong cross-cleavage. Very little free lead oxide, if any, was present. The material was practically all of the anomalous blue interference color referred to in the account of the 69 equivalent – per cent. preparation. Some grains approached a yellow interference color, but all gave the colored bars, usually blue, and all behaved as uniaxial negative.

b. Crystal fragments of preparations still richer in lead oxide have less of the anomalous blue, but free lead oxide appears in an increasing proportion.

Conclusion from the Optical Analysis.—The preparation corresponding to the composition $3PbO : 1SiO_2$ is homogeneous and seems to be an individual compound. It is optically anomalous.

5. Lead oxide and silica, the end members of the series, are well characterized in the literature.[1] *Lead oxide* appears under the microscope to be slightly pleochroic and to have a conspicuous angular cleavage. Its interference figure is biaxial with positive character. The indices of refraction are very high. *Quartz* is recognized by its low indices of refraction and weak double refraction. It is sometimes hexagonal in outline and shows a positive uniaxial interference figure.

Thermal Analysis.—The further study of the thermal analysis has revealed little of interest. The melting-point curve remains very much as shown in Fig. III of the preceding article.[2] It is reproduced here (Fig. II) with a slight modification for the 75 equivalent – per cent. composition. The relationships in the neighborhood of both minima are not understood.

The various heating curves for the individual mixtures show that changes of phase occur below the apparent eutectic point and, further, that the kind of phases formed on cooling depend on the manner of cooling, as in many other systems. In order to study these changes thermally it would be necessary to cool and melt in such a way as to fix a definite phase. The cooling would be easy, but we have as yet no means of

[1] Groth: Chemische Krystallographie, **1906**, I, 76, 86.
[2] This Journal, **42**, 472.

identifying the various solid phases (crystallized substances), the usual method of utilizing refractive index being inapplicable on account of the high indices of the lead compounds. The discovery of a liquid with an index of refraction approximating 2 would be of great value.

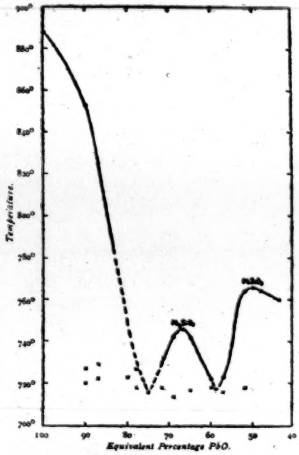

Fig. II
Melting-point Curve (dotted portions uncertain)

That the preparations $1PbO : 1SiO_2$ and $2PbO : 1SiO_2$ are compounds is shown clearly by the well-defined maxima of the melting-point curve. The concordance of the conclusions from the thermal and optical analyses may be taken as satisfactory proof that these compounds exist and are stable in the presence of the melt. The existence of the 1 : 1 compound as a mineral proves its stability at ordinary temperatures.

As to the 3 : 2 preparation, little can be told from the thermal analysis. There appears to be a crystallographic inversion point a few degrees below the melting point, for the

heating curve shows two steps close together; several mixtures of adjacent composition, however, exhibit three steps. No artificial preparation of the 3 : 2 composition that has been studied was found to be entirely homogeneous.

For the 3 : 1 preparation no maximum has been found, either, but the melting point of the preparation is the sharpest, most constant and most easily reproducible of the whole series. This adds to the probability, established by the optical analysis, that we are dealing with a homogeneous individual, namely, the compound Pb_3SiO_5.

GENERAL CONCLUSION

As a result of further thermal analysis of the system PbO-SiO_2 and a careful optical analysis of the same preparations, as well as of the minerals pertaining to this system, we regard the existence of the compounds 1 : 1, 2 : 1 and 3 : 2 as satisfactorily established. The properties of the 1 : 1 and 3 : 2 compounds correspond to those of the minerals alamosite and barysilite, respectively. These minerals have thus been synthesized in the laboratory, the alamosite, indeed, before it was found in nature. The phenomena attending the melting of the 3 : 2 substance are too complicated to be understood, but the optical evidence is regarded as convincing that we are dealing with a simple compound. The sharp melting point and peculiar optical character under the microscope of the 3 : 1 preparation render the existence of such a compound very probable, but the melting-point curve gives no evidence thereof. The lead silicate found under lead smelters appears to be a complex and variable solid solution of variable and difficultly definable crystallographic properties. A comparison of this system with the systems of the calcium,[1] manganese[2] and lithium[3] silicates, respectively, reveals extensive analogy in the formulas and relative stability of the compounds in contact with the melt. In all of these systems the ortho and meta compounds are well defined, while to the possible 3 : 2 and 3 : 1 compounds more or less un-

[1] Shepherd and Rankin: J. Ind. Eng. Chem., **3**, 211.
[2] Doerinckel: Metallurgie, **8**, 201.
[3] Rieke and Endell: Sprechsaal, **43**, 683. VanKlooster: Z. anorg. Chem., **69**, 135.

certainty is attached because of eutectic and inversion relationships.

THE AMMONIA SYSTEM OF ACIDS, BASES AND SALTS

By Edward C. Franklin

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IV. *Conclusion.*

I. INTRODUCTION

1. The Properties of Liquid Ammonia.—The many striking analogies between liquid ammonia and water as electrolytic solvents have been emphasized by the writer and his coworkers in papers which have appeared from time to time during the past decade. In all those properties which give to water its unique position among solvents, such as its abnormally high boiling point, its high specific heat, its high heat of volatilization, its high critical temperature and pressure, its high association constant, its high dielectric constant, and its low boiling-point elevation constant, its power as an electrolytic solvent, and the facility with which it forms compounds with salts, liquid ammonia shows a remarkable similarity to water.

While the boiling point of liquid ammonia is 33°.46 below zero,[1] it still appears abnormally high when compared with the boiling temperatures of phosphine, arsine, stibine, methane, ethylene, hydrogen sulphide, hydrochloric acid, etc. The specific heat of liquid ammonia[2] and the heat of fusion[3] of the solid are

[1] Gibbs: J. Am. Chem. Soc., **27**, 851 (1905). Cf. Franklin: Ann. Physik, [4] **24**, 367 (1907).

[2] Elleau and Ennis: J. Frank. Inst., **145**, 189 (1898). Dieterici: Z. Kälteind., **1904**.

[3] Fourcrand and Massol: Compt. rend., **134**, 653, 743 (1902).

greater than the corresponding constants for water or any other known substance, while its heat of volatilization,[1] with the one exception of water, is the highest of any known liquid. The critical temperature of ammonia is abnormally high, and its critical pressure—the more characteristic constant—is higher than that of any other liquid excepting water. Ammonia is an associated liquid,[2] and its dielectric constant,[3] though much below that of water, is still high when compared with that of nonelectrolytic solvents. Its boiling-point elevation constant is the lowest of any known liquid, namely, 3.4,[4] as compared with 5.2 for water. In its tendency to unite with salts and other compounds, it probably exceeds water, since salts with ammonia of crystallization are perhaps even more numerously recorded in the literature than are salts with water of crystallization. As a solvent for salts it is generally much inferior to water,[5] though some salts, for example the iodides and bromides of mercury, lead and silver, dissolve very much more abundantly in ammonia than they do in water, and it far surpasses the latter solvent in its ability to dissolve the compounds of carbon. Finally it exhibits conspicuous power as an ionizing solvent,[6] the more dilute

[1] Elleau and Ennis: *Loc. cit.* Franklin and Kraus: J. Phys. Chem., **11**, 553 (1907). Dieterici: *Loc. cit.*

[2] Franklin and Kraus: THIS JOURNAL, **21**, 14 (1899). Walden: Z. physik. Chem., **70**, 599 (1911).

[3] Goodwin and Thompson: Phys. Rev., **8**, 38 (1899). Coolidge: Wied. Ann., **69**, 125 (1899).

[4] Franklin and Kraus: THIS JOURNAL, **20**, 836 (1898).

[5] Franklin and Kraus: *Ibid.*, **20**, 820 (1898).

[6] Cady: J. Phys. Chem., **1**, 707 (1897). Franklin and Kraus: THIS JOURNAL, **23**, 277 (1900). Franklin and Cady: J. Am. Chem. Soc., **26**, 499 (1904). Franklin and Kraus: *Ibid.*, **27**, 191 (1905). Franklin: Z. physik. Chem., **69**, 272 (1909).

It will be observed that it is the hydrides of the first or typical members of the fifth and sixth groups of the Periodic System which show conspicuous power as electrolytic solvents. The hydrides of the other members of these groups (hydrogen sulphide, phosphorus hydride, etc.) show scarcely a trace of such properties. Of the members of the seventh group, Steele, Archibald and MacIntosh have shown that hydrochloric acid, hydrobromic acid and hydriodic acid show some considerable power of forming electrolytic solutions. Such relationships, together with the fact that the discovery of fluorine was made possible to Moissan by the observation that potassium fluoride dissolves in liquid hydrofluoric acid to form a conducting solution, suggests that hydrofluoric acid may be as powerful, or possibly even more powerful an ionizing agent than water itself. Some of these considerations, together with the facts of its abnormally high boiling point, its evident association even in the gaseous state, its power of uniting with fluorides as hydrofluoric acid of crystallization, led the writer, some years ago, to make some preliminary experiments on liquid hydrofluoric acid

ammonia solutions at 33°.5 being very much better conductors of electricity than aqueous solutions of the same concentration at 18°.

II. METATHETIC REACTIONS BETWEEN ORDINARY ACIDS, BASES AND SALTS IN LIQUID AMMONIA SOLUTIONS

2. Reactions between Salts.—The general resemblance between ammonia and water, outlined above, led Franklin and Kraus to inquire whether ordinary metathetic reactions take place in the former solvent as they do in the latter. Such was found to be the case,[1] with the interesting difference that, as a result of variations in the order of solubilities in ammonia as compared with water, certain reactions take place in the former solvent which do not occur in the latter, or they may even proceed in opposite directions in the two solvents. As examples may be mentioned the separation of the sulphides of the alkaline earths as white precipitates when liquid ammonia solutions of soluble salts of these metals and ammonium sulphide are brought together, and the precipitation of an alkaline-earth chloride when a solution of a soluble salt of any one of these metals is acted upon by a solution of a soluble chloride. The equation

$$2AgNO_3 + BaCl_2 = Ba(NO_3)_2 + 2AgCl$$

read from left to right, represents the familiar action between silver nitrate and barium chloride in aqueous solution. Read from right to left it represents the action of silver chloride on barium nitrate in solution in liquid ammonia. Barium chloride is but slightly soluble in liquid ammonia, while the other three salts are readily soluble.

3. Reactions between Acids and Bases.—At first thought it may seem absurd to speak of acids existing in ammonia solu-

in the hope that he might see his way to a more extended investigation of liquid hydrofluoric acid as an electrolytic solvent. These preliminary experiments on anhydrous hydrofluoric acid showed it to possess strong solvent powers. Potassium fluoride, sodium fluoride, potassium chloride, sodium bromide, sodium nitrate, sodium chlorate, potassium bromate, acetamide, urea and potassium sulphate are abundantly soluble; silver cyanide, barium fluoride and copper chloride appear to dissolve to some extent; while calcium fluoride, copper sulphate, copper nitrate, ferrous chloride, mercuric oxide, lead fluoride and metallic magnesium are insoluble.

[1] THIS JOURNAL, **21**, 1 (1899).

tions and reacting therein with bases. Ammonia is frequently referred to as a base, and every one knows that acids unite with ammonia to form the familiar ammonium salts. The fact, however, is to be emphasized that ammonia is not a base, that it is only in the presence of water that ammonia exhibits basic properties, and that in consequence the dry liquid behaves almost, if not quite, as indifferently as water itself towards the ordinary indicators. Now it is an important fact that many ammonium salts of both oxygen acids and halogen acids dissolve freely in the liquid ammonia to form solutions which show certain truly acid properties, as follows: first, they discharge the red color of liquid ammonia solutions of phenolphthalein which have been rendered alkaline by the addition of a small quantity of a base; second, solutions of ammonium salts in ammonia attack sodium, potassium, calcium, magnesium, zinc and cadmium, with the evolution of hydrogen and the formation of the respective metallic salts in accordance with the general equation

$$M + NH_4Ac = MAc + NH_3 + H$$

third, many metallic oxides and certain basic salts—all the members of which two classes of compounds are practically insoluble in ammonia—dissolve in liquid ammonia solutions of ammonium salts. For example, Divers[1] found sodium hydroxide, potassium hydroxide and the oxides of cobalt, copper, lead, magnesium, mercury, cadmium and zinc to be soluble in liquid ammonia solutions of ammonium nitrate.[2] The writer has confirmed most of these results of Divers and has also observed the solubility of some of these hydroxides and oxides in solutions of ammonium salts other than the nitrate. It therefore appears that bases dissolve in ammonia solutions of ammonium salts[3] in a manner analogous to the

[1] Phil. Trans., **163**, 359 (1873).

[2] The so-called Divers' liquid, it is to be observed, is simply a concentrated solution of ammonium nitrate in liquid ammonia. The fact that the solution exists at ordinary temperatures at atmospheric pressure is explained as the result of the lowering of the vapor tension of the solvent by the large amount of ammonium nitrate in solution. Kurilloff: Z. physik. Chem., **25**, 108 (1898). Divers: *Ibid.*, **28**, 430 (1898).

[3] The acid properties of ammonium salts in liquid ammonia solutions thus made evident suggest that, analogously, in water solutions of hydrochloric acid the hydrogen ion may be associated with water as OH_3^+. Three hydrates of hydrochloric acid

solution of insoluble bases in aqueous acid solutions, as indicated, for example, by the familiar equations

$$NaOH + NH_4Cl = NaCl + H_2O + NH_3$$
$$Ca(OH)_2 + 2NH_4NO_3 = Ca(NO_3)_2 + 2H_2O + 2NH_3$$

for two of the above mentioned bases.

Even in water solutions the acid properties of ammonium salts are frequently in evidence, as, for example, in the well known cases of the solubility of metallic zinc and magnesium, and of certain metallic oxides, hydroxides and carbonates, in aqueous solutions of ammonium salts. Especially interesting and significant in this connection, as will be discussed in detail in a subsequent paper, is the conversion of the so-called mercuriammonium compounds into normal mercuric salts by the action of ammonium salts in aqueous solutions.

The reactions which have just been described as taking place in liquid ammonia differ in no essential respects from the familiar metathetic reactions in aqueous solutions. They are reactions between the ordinary oxygen acids, bases and salts and the halogen acids and salts, taking place in a solvent other than water, a field of study that has received considerable attention from Neumann and his students.[1]

III. ACIDS, BASES AND SALTS OF THE AMMONIA SYSTEM

4. Compounds Related to Ammonia as the Ordinary Oxygen Acids, Bases and Salts are Related to Water.—A consideration of the many points of resemblance between water and liquid ammonia as electrolytic solvents has led the writer to the conception of a system of acids, bases and salts in which ammonia occupies a position similar to that held by water in its relation to the ordinary oxygen acids, bases and salts. The compounds bearing such a relationship to ammonia are the acid amides and imides, the metallic amides and imides and the

of the respective formulas $HCl.3H_2O$, $HCl.2H_2O$ and $HCl.H_2O$ are known (Rupert: J. Am. Chem. Soc., **31**, 851). Of the latter compound it is interesting to note that Rupert reports it as a "white, crystalline substance resembling ammonium chloride in general character."

[1] Ber. d. chem. Ges., **43**, 313 (1910). Rohland: Z. anorg. Chem., **18**, 322 (1898).

metallic derivatives of the acid amides and imides, respectively. Just as acetic acid, for example, may be looked upon as a derivative of water in which one-half of the hydrogen is replaced by the electronegative radical, acetyl, so acetamide is ammonia in which one-third of the hydrogen is replaced by acetyl; as potassium hydroxide is a derivative of water, so is potassium amide a similar derivative of ammonia; and in the same sense that potassium acetate is derived from water, so potassium acetamide may be regarded as ammonia in which a part of the hydrogen is replaced by potassium and another part by the acetyl group. Finally, the familiar relations existing between the metallic hydroxides and oxides and between acids and acid anhydrides are exemplified, at least formally, in the analogous relationship which the metallic amides and imides, on the one hand, bear to the metallic nitrides, and which the acid amides and imides, on the other hand, bear to the nonmetallic nitrides.

5. *Nomenclature.*—The ordinary acids, bases and salts, which were first recognized by Lavoisier as being oxygen compounds, came later to be looked upon as derivatives of water, and as such constituting what may be called a water system of acids, bases and salts. Under the influence of the dictum of Lavoisier that oxygen is a never-failing constituent of all acids, chemists assumed that hydrochloric acid, the one known halogen acid, was a hydrated oxide of an unknown element; and it was only after the demonstration of the elementary nature of iodine and chlorine that a class of oxygen-free acids and salts—the halogen acids and salts—came to be clearly recognized. Latterly a limited number of other oxygen-free compounds have come to be recognized as possessing the properties of acids, bases and salts, conspicuous among them being the sulpho acids, bases and salts. Certain acid amides have long been known to possess acid properties to the extent, at least, of forming saltlike metallic derivatives, but it is only since the investigations of the writer and his collaborators have demonstrated the acid, basic and saltlike character of the acid amides, the metallic amides and the metallic derivatives of the acid amides, respectively, that the existence of

an ammonia system of acids, bases and salts must be recognized.

Since it will be frequently necessary in the course of this article to speak of the acids, bases and salts of this system and to describe a considerable number of reactions between these ammonia derivatives, it becomes desirable to formulate a scheme of nomenclature in order that the discussions which follow may be carried on as clearly and concisely as possible. A brief statement of the system of nomenclature which will be used is given herewith.

1. The author has already proposed[1] to designate the acids, bases and salts of the ammonia or nitrogen system as *ammono acids*, *ammono bases* and *ammono salts*, respectively, which is to say that the acid amides and imides, including the amides and imides of the nonmetallic elements, are ammono acids, the metallic amides and imides are ammono bases, and the metallic derivatives of the acid amides and imides are ammono salts.[2]

2. When it becomes desirable to distinguish between the acids, bases and salts of the ammonia system, on the one hand, and those of the oxygen or water system on the other, it will be convenient to refer to the members of the latter system as *aquo acids*, *aquo bases* and *aquo salts*.[3]

3. We shall find that compounds exist which are related to ammonia as the ordinary acid salts and basic salts—that is to say, the aquoacid salts and the aquobasic salts—are related to water. Such compounds will be called ammonoacid

[1] J. Am. Chem. Soc., **27**, 823 (1905).

[2] Acetamide and diacetamide are accordingly ammonoacetic acids; the potassium derivatives of acetamide and sodium diacetamide are ammonoacetates of potassium and sodium, respectively. Urea is ammonocarbonic acid and the potassium derivatives of urea obtained by Franklin and Stafford are potassium ammonocarbonates. Trinitroaniline is ammonopicric acid. Calcium cyanamide is the calcium salt of ammonocyanic acid.

[3] The writer in another place (*loc. cit.*) has proposed the prefix hydro for the oxygen acids, bases and salts but submits that the word aquo, which he encountered in the writings of Werner (Neuere Anschauungen auf dem Gebiete der anorganischen Chemie) is a much better designation. The generally accepted practice of referring to the aquo acids, bases and salts as oxygen acids, bases and salts would require us to designate the analogous derivatives of ammonia as nitrogen acids, bases and salts, a procedure which is open to obvious objections.

salts and ammonobasic salts,[1] respectively, and the process whereby the ammonobasic salts are formed will be called *ammonolysis*. It will be shown that ammonolytic reactions take place in liquid ammonia solutions in a manner entirely analogous to the familiar hydrolytic reactions in water solutions.

4. We shall also have occasion to speak of compounds which are related to ammonia as the ordinary hydrated salts, or salts with water of crystallization, are related to water. Obviously such compounds may very properly be called *ammonates*, just as salts with water of crystallization are sometimes called hydrates, or they may be called either *ammonated salts* or *salts with ammonia of crystallization*.[2]

5. Furthermore, when it becomes desirable to emphasize the distinction between a water-free salt and a salt with water of crystallization or containing adsorbed water, the former is usually referred to as the anhydrous salt. Similarly, when it is desired to speak of ammonia-free salts, in contradistinction to a salt containing ammonia, either adsorbed or as ammonia of crystallization, it will be convenient to speak of the former as *deammonated salts* or as *anammonous salts*.[3]

6. The relationship which the bases of the water system bear to the metallic oxides, on the one hand, and those which the acids bear to their anhydrides, on the other, are found to be exemplified by the relationship which exists between the acid amides and imides and the nitrides of the nonmetallic elements or electronegative radicals, and between the metallic or basic amides and imides and the metallic nitrides. We

[1] Not basic ammono salts and acid ammono salts. The formulas for three ammonobasic salts are NH_2HgCl, NH_2HgNO_3 and $NH_2HgNH(CH_3CO)$; the first formula represents an ammonobasic halogen salt, the well-known infusible white precipitate; the second represents an ammonobasic aquo salt, a compound which has been recently prepared [Strömholm: Z. anorg. Chem., **57**, 72 (1908)] and the third represents an ammonobasic ammono salt, a compound not known to exist but which may possibly be prepared by the action of potassium amide on acetamide mercury. An ammono salt may be expected to undergo either ammonolysis to form an ammonobasic ammono salt, such as represented by the last formula above, or hydrolysis to form an aquobasic ammono salt, such as represented by the formula $HCONHHgOH$, a compound which has been prepared by Fischer and Grützner [Arch. Pharm., **233**, 329 (1894)].

[2] These designations have frequently been used by others.

[3] A designation first used in print by Browne and Houlehan: Science, **34**, 284 (1911).

I

THE WATER OR OXYGEN SYSTEM *Aquo Acids and Acid Anhydrides*		THE AMMONIA OR NITROGEN SYSTEM *Ammono Acids and Acid Nitrides*	
Acetic acid	CH_3COOH	Acetamide	CH_3CONH_2
		Diacetamide	$(CH_3CO)_2NH$
Acetic anhydride	$(CH_3CO)_2O$	Triacetamide	$(CH_3CO)_3N$
Benzoic acid	C_6H_5COOH	Benzamide	$C_6H_5CONH_2$
Benzenesulphonic acid	$C_6H_5SO_2OH$	Benzenesulphonamide	$C_6H_5SO_2NH_2$
Nitrobenzenesulphonic acid	$C_6H_4(NO_2)SO_2OH$	Nitrobenzenesulphonamide	$C_6H_4(NO_2)SO_2NH_2$
Nitric acid	NO_2OH	Nitramide	NO_2NH_2
Sulphuric acid	$SO_2(OH)_2$	Sulphamide	$SO_2(NH_2)_2$
		Sulphimide	$(SO_2NH)_3$
Carbonic acid	$CO(OH)_2$	Carbamide	$CO(NH_2)_2$
		Nitrourea	$NH_2CONH(NO_2)$
		Guanidine	$HNC(NH_2)_2$
		Nitroguanidine	$NH_2C(NH)NHNO_2$
		Parabanic acid	$C_3O_3(NH)_2$
		Uric acid	$C_5O_3(NH)_4$
Cyanic acid	CNOH	Cyanoamide	$CNNH_2$
Picric acid	$C_6H_2(NO_2)_3OH$	Picramide	$C_6H_2(NO_2)_3NH_2$
Orthosilicic acid	$Si(OH)_4$	Silicon amide	$Si(NH_2)_4$
		Silicon imide	$Si(NH)_2$
Silicic anhydride	SiO_2	Silicon nitride	Si_3N_4

THE WATER OR OXYGEN SYSTEM

Aquo Bases and Basic Oxides

Sodium hydroxide	$NaOH$
Lithium hydroxide	$LiOH$
Lithium oxide	Li_2O
Calcium hydroxide	$Ca(OH)_2$
Magnesium oxide	MgO
Mercuric oxide	HgO
Bismuth oxide	Bi_2O_3

THE WATER OR OXYGEN SYSTEM

Aquo Salts

Potassium acetate	CH_3COOK
Magnesium acetate	$(CH_3COO)_2Mg$
Potassium benzenesulphonate	$C_6H_5SO_2OK$
Potassium sulphate	$KOSO_2OK$

II

THE AMMONIA OR NITROGEN SYSTEM

Ammono Bases and Basic Nitrides

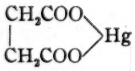
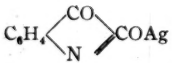
Sodium amide	$NaNH_2$
Lithium amide	$LiNH_2$
Lithium imide	Li_2NH
Lithium nitride	Li_3N
Calcium amide	$Ca(NH_2)_2$
Magnesium nitride	Mg_3N_2
Mercuric nitride	Hg_3N_2
Bismuth nitride	BiN

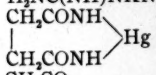
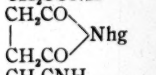
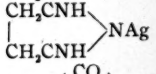
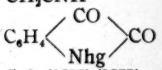
III

THE AMMONIA OR NITROGEN SYSTEM

Ammono Salts

Monopotassium acetamide	CH_3CONHK
Dipotassium acetamide	CH_3CONK_2
Sodium diacetamide	$(CH_3CO)_2NNa$
Magnesium acetamide	$(CH_3CONH)_2Mg$
Monopotassium benzenesulphonamide	$C_6H_5SO_2NHK$
Dipotassium benzenesulphonamide	$C_6H_5SO_2NK_2$

Potassium acid sulphate	$HOSO_2OK$
Potassium carbonate	$KOCOOK$
Potassium acid carbonate	$HOCOOK$
Mercuric succinate	
Isatin silver[1]	
Mercury cyanurate[2]	$(CN)_3(Ohg)_3$

Dipotassium sulphamide	$KHNSO_2NHK$
Monopotassium sulphamide	H_2NSO_2NHK
Dipotassium urea	$KHNCONHK$
Monopotassium urea	$H_2NCONHK$
Potassium nitrourea	$H_2NCONKNO_2$
Potassium nitroguanidine	$H_2NC(NH)NKNO_2$
Mercuric succinamide	
Mercuric succinimide	
Silver succinimidine	
Isatin mercury[1]	
Potassium parabanate	$C_3O_3(NH)(NK)$
Calcium cyanoamide	$CNNCa$
Mercuric isocyanurate[2]	$(CO)_3(Nhg)_3$

[1] Peters: Ber. d. chem. Ges., **40**, 235 (1907).
[2] Hantzsch: *Ibid.*, **35**, 2717 (1902).

The Water or Oxygen System

Amphoteric Hydroxides

Zinc hydroxide	$Zn(OH)_2$
Lead hydroxide	$Pb(OH)_2$

Salts of Amphoteric Hydroxides

Potassium zincate	
Potassium plumbite	
Potassium stannate	$KOSnOOK.3H_2O$

Aquobasic Salts

Basic mercuric fluoride	$HgOHgFl_2.H_2O$
Basic mercuric chlorides	$Hg_xO_yCl_z$
Basic mercuric bromide	$Hg_4O_3Br_2$
Basic lead iodides	$xPbI_2.yPbO$

IV

The Ammonia or Nitrogen System

Amphoteric Amides, Imides and Nitrides

Zinc amide	$Zn(NH_2)_2$
Silver amide	$AgNH_2$
Lead imide	$PbNH$
Cuprous nitride	Cu_3N
Thallium nitride	Tl_3N

V

Salts of Amphoteric Amides and Imides

Potassium ammonozincate	$KHNZnNKH.2NH_3$
Potassium ammonoplumbite	$PbNK.2\frac{1}{2}NH_3$
Potassium ammonostannate	$KNSnNK.4NH_3$ or $K_2Sn(NH)_3.3NH_3$

VI

Ammonobasic Salts

Basic mercuric chlorides	NH_2HgCl $NH_2HgCl.HgCl_2$ $(Hg_2NCl)_2.HgCl_2$
Basic mercuric bromides	NH_2HgBr $(Hg_2NBr)_4.HgBr_2$ $NH(HgBr)_2$ Hg_2NBr
Basic lead iodide	$Pb_2NI.2NH_3$

shall therefore on occasion refer to the nonmetallic nitrides as *acid nitrides*, or *acid anammonides*, and to the metallic nitrides as *basic nitrides*.

7. Finally, as there are amphoteric hydroxides and oxides, so we shall find it convenient to speak of those ammonia derivatives which show amphoteric properties as *amphoteric amides*, *imides* and *nitrides*.

In the tables above is given a selected list of compounds belonging to the water and ammonia systems, respectively.

6. Ammono Acids.—The acid amides and imides derived from organic acids constitute a group of well known compounds, since practically every known carboxylic and sulphonic acid furnishes such a derivative. The amides and imides of the inorganic acids are not so well known, although in recent years several such compounds have been prepared and studied, among others especially the amides of sulphuric[1] and nitric[2] acids and the amides and imides of the acids of phosphorus.[3]

The members of the large group of acid amides and imides, in so far as they are soluble, give solutions in liquid ammonia which discharge the color of alkaline solutions of phenolphthalein,[4] conduct the electric current, dissolve certain metals, and react with metallic amides, in a manner described in detail below, to give representatives of the class of ammono salts. The strength of these ammono acids, if it be assumed that their strength is indicated by the conductivity of their solutions in liquid anmmonia and by the extent to which their salts resist the hydrolytic action of water, varies through quite as wide limits as do the ordinary oxygen acids. Acetamide and carbamide, at one extreme, for example, form solutions in liquid ammonia which have scarcely

[1] Traube: Ber. d. chem. Ges., **25**, 2472 (1892); **26**, 610 (1893). Hantzsch and Holl: *Ibid.*, **34**, 3435 (1901). Ruff: *Ibid.*, **36**, 2900 (1903). Franklin and Stafford: THIS JOURNAL, **28**, 95 (1902). Franklin and Kraus: J. Am. Chem. Soc., **27**, 191 (1905). Franklin: Z. physik. Chem., **69**, 300 (1909).

[2] Thiele and Lachmann: Ann. Chem. (Liebig), **288**, 267 (1895). Franklin and Kraus: J. Am. Chem. Soc., **27**, 191 (1905).

[3] Stokes: THIS JOURNAL, **1893-1898**.

[4] A large excess of such an acid as acetamide is required to discharge the red color of a solution of phenolphthalein which has been rendered alkaline by potassium amide, obviously for the reason that acetamide is a very weak acid whose salts in solution in liquid ammonia are highly ammonolyzed.

more than an appreciable conductivity, and their potassium salts are completely hydrolyzed in the presence of water. Toward the other extreme may be mentioned such ammono acids as phthalimide, nitrobenzenesulphonamide, nitrourethane, nitroguanidine, saccharin, etc., which dissolve in ammonia to form good conducting solutions,[1] and which form salts of the alkali metals which are more or less stable in the presence of water.

Further compounds which are to be included among the ammono acids are the amides and imides of the nonmetallic elements. Just as the halogen derivatives of the strongly electronegative elements, such as arsenic, phosphorus, boron, silicon, are completely hydrolyzed by the action of water, so we may expect the same compounds to undergo decomposition in contact with liquid ammonia, with the formation of products bearing relations to this solvent analogous to those which the hydrolytic products bear to water.

The following equations, giving the results of recent work, show that in fact such ammonolytic reactions take place:

$3TeCl_4 + 16NH_3 = Te_3N_4 + 12NH_4Cl$[2]
$B_2S_3 + 6NH_3 = B_2(NH)_3 + 3NH_4SH$[3]
$BCl_3 + 6NH_3 = B(NH_2)_3 + 3NH_4Cl$[4]
$PCl_5 + 5NH_3 = P(NH)NH_2 + 3NH_4Cl$[5]
$AsCl_3 + 6NH_3 = As(NH_2)_3 + 3NH_4Cl$[6]
$SiCl_4 + 8NH_3 = Si(NH_2)_4 + 4NH_4Cl$[7]
$SiS_2 + 4NH_3 = Si(NH)_2 + 2NH_4SH$[8]
$SiSBr_2 + 4NH_3 = SiS(NH_2)_2 + 4NH_4Br$[9]

Tellurium nitride, Te_3N_4, is an acid nitride or an acid anammonide; boron imide, $B_2(NH)_3$, and boron amide, $B(NH_2)_3$, are ammonoboric acids; phosphorous imide amide, $NH=P.NH_2$, is an ammonophosphorous acid; arsenious amide, $As(NH_2)_4$, is an ammonoarsenious acid; silicon amide, $Si(NH_2)_4$,

[1] Franklin and Kraus: J. Am. Chem. Soc., **27**, 191 (1905).
[2] Metzner: Compt. rend., **124**, 32 (1897).
[3] Stock and Blix: Ber. d. chem. Ges., **34**, 3039 (1901).
[4] Joannis: Compt. rend., **135**, 1106 (1903).
[5] Joannis: *Ibid.*, **139**, 364 (1904).
[6] Hugot: *Ibid.*, **139**, 54 (1904).
[7] Lengfeld: THIS JOURNAL, **21**, 531 (1899). Vigouroux and Hugot: Compt. rend., **136**, 1670 (1903).
[8] Blix and Wirbelauer: Ber. d. chem. Ges., **36**, 4220 (1903).
[9] Blix: *Ibid.*, **36**, 4219 (1903).

and silicon imide, $Si(NH)_2$, are ammonosilicic acids; and sulphosilicourea, $SiS(NH_2)_2$, is a sulphoammonosilicic acid. As is pointed out below, at least some of these ammono acids may be expected to react with potassium amide to give the corresponding potassium ammono salts.

Representatives of still another class of ammono acids are the nitroanilines which are related to ammonia as the nitrophenols are related to water. Just as the acid properties and electrical conductivities of aqueous solutions of the nitrophenols increase rapidly with the number of nitro groups present in the benzene ring, so in the case of the nitroanilines it has been found that while ammonia solutions of aniline are practically nonconductors, dinitroaniline gives a solution which is a good conductor and trinitroaniline forms solutions which approach the salts in the facility with which they convey the electric current.[1] Metallic derivatives of trinitroaniline have not been prepared, although Franklin and Stafford have shown[2] the probable existence of a potassium salt.

It is interesting in this connection to note other and similarly marked strengthening of the acid properties of certain acid amides by the introduction of negative groups. For example, liquid ammonia solutions of acetamide, urea and urethane are very poor conductors, while cyanoacetamide, nitroguanidine, and especially nitrourethane,[3] form solutions which are excellent conductors. As was pointed out above, some of these ammono acids form salts which are stable in aqueous solutions, and in consequence have been prepared in considerable number in the past.

7. *Ammono Bases.*—The metallic amides, imides and nitrides constitute a group of substances by no means so numerously represented among known compounds as is the case with the ammono acids. And among those that are known, as with the aquo bases it is the hydroxides of the alkali metals only which are soluble to any extent in water, so it is the amides of the alkali metals which are soluble in ammonia.

[1] J. Am. Chem. Soc., **27**, 197 (1905).
[2] This Journal, **28**, 102 (1902).
[3] Franklin and Kraus: J. Am. Chem. Soc., **27**, 205 (1905).

Indeed, among the ammono bases potassium amide only (probably also rubidium and caesium amides) is abundantly soluble.

Potassium amide has long been known, having been first prepared by Gay-Lussac and Thénard[1] by heating metallic potassium in contact with gaseous ammonia. It is most conveniently prepared by the action of liquid ammonia on the metal in the presence of platinum black. The reaction between the metal and ammonia, which otherwise takes place very slowly,[2] is so greatly accelerated by the presence of the catalyzer[3] that any quantity of the amide may thus be very easily made. Potassium amide crystallizes from cold, concentrated liquid ammonia solutions in the form of beautiful, colorless leaflets. Its solutions in liquid ammonia are good conductors of electricity.[4] The basic properties of potassium amide are shown by its behavior toward liquid ammonia solutions of phenolphthalein, and by its action on liquid ammonia solutions of oxygen acids, halogen acids and ammono acids, and also by its action on metallic zinc. Its behavior toward oxygen acids and halogen acids is represented by the equations

$$KNH_2 + NH_4NO_3 = KNO_3 + 2NH_3$$
$$KNH_2 + NH_4Cl = KCl + 2NH_3$$

The action of potassium amide on the ammono acids and on metallic zinc is discussed in some detail further on in this paper.

Taking advantage of the solubility of potassium amide, the writer has been able to prepare a number of insoluble metallic derivatives of ammonia by bringing soluble metallic salts and potassium amide together in liquid ammonia solutions.[5] The new substances are thus obtained as precipitates which may be purified and analyzed and their identity thereby established. It has been found that potassium amide in ammonia solution reacts with silver nitrate to form silver amide, with lead ni-

[1] Recherches physico-chimiques, **1**, 337 (1811).
[2] Joannis: Compt. rend., **112**, 502 (1891).
[3] Franklin: J. Am. Chem. Soc., **27**, 831 (1905).
[4] Franklin: Z. physik. Chem., **69**, 290 (1909). Arrhenius' Jubelband.
[5] J. Am. Chem. Soc., **27**, 833 (1905).

trate or iodide to form lead imide, with mercuric bromide and iodide to form mercuric nitride, and with bismuth bromide and iodide to form bismuth nitride. These reactions are represented by the following equations:

$$AgNO_3 + KNH_2 = AgNH_2 + KNO_3$$
$$Pb(NO_3)_2 + 2KNH_2 = PbNH + 2KNO_3 + NH_3$$
$$3HgI_2 + 6KNH_2 = Hg_3N_2 + 6KI + 4NH_3$$
$$BiBr_3 + 3KNH_2 = BiN + 3KBr + 2NH_3$$

The close analogy between these reactions carried on in liquid ammonia solutions and the corresponding reactions in the water system will be clear from a comparison of the above equations with the following:

$$2AgNO_3 + 2KOH = Ag_2O + 2KNO_3 + H_2O$$
$$Pb(NO_3)_2 + 2KOH = PbO.xH_2O + 2KNO_3 + (1-x)H_2O$$
$$HgCl_2 + 2KOH = HgO + 2KCl + H_2O$$
$$2BiCl_3 + 6KOH = Bi_2O_3.xH_2O + 6KCl + (3-x)H_2O$$

Just as in water solutions it is sometimes the hydroxide and at other times the oxide which is obtained, so in the case of the action of potassium amide on a silver salt in liquid ammonia it happens to be the amide which is formed; lead salts under similar treatment happen to give the imide, a deammonation product of the amide; while mercury and bismuth salts give neither the amide nor imide but in their stead the final deammonation product, the nitride.

In addition to the four ammono bases prepared as described above, Fitzgerald[1] has shown that potassium amide acts upon cupric nitrate in solution in liquid ammonia to form cuprous nitride in accordance with the equation

$$3Cu(NO_3)_2 + 6KNH_2 = Cu_3N + 6KNO_3 + N + 4NH_3$$

and it has been recently shown in this laboratory that a nitride of thallium is formed after the manner represented by the equation[2]

$$3TlNO_3 + 3KNH_2 = Tl_3N + 3KNO_3 + 2NH_3$$

The new ammono bases thus obtained are insoluble in liquid ammonia, but dissolve readily in ammonia solutions of appro-

[1] J. Am. Chem. Soc., **29**, 656 (1907).
[2] Experimental results not yet published.

priate ammonium salts. Four of them—silver amide, lead imide, cuprous nitride and thallium nitride—are amphoteric in character, for in addition to being soluble in ammonium salts, that is, in acids, they are also soluble in solutions of potassium amide. When dry, they all explode with more or less violence when heated or subjected to shock. Silver amide especially is so sensitive that it was only by exercising the greatest care that the isolation and analysis of the substance were accomplished. With the exception of mercuric nitride, they are completely hydrolyzed by the action of water with the evolution of ammonia and the formation of aquo bases. This exceptional behavior of mercuric nitride is significant, as will be discussed in detail in a subsequent paper.

Soluble salts of a number of other metals, including calcium, barium, aluminium, ferrous and ferric iron, cadmium, magnesium, platinum and nickel, have been found to give precipitates when treated in liquid ammonia solutions with potassium amide. It therefore appears certain that by this method a very considerable number of new metallic amides, imides and nitrides may be prepared.

Before leaving the subject of the ammono bases it may be worth while to state that attempts have been made to prepare amides of the formulas $(CH_3)_4N.NH_2$, $(CH_3)_3S.NH_2$ and $(C_6H_5)_2I.NH_2$ by the action of potassium amide on tetramethylammonium chloride, trimethylsulphonium iodide and diphenyliodonium iodide, respectively, but as yet without success.

Other ammono bases which have been prepared and are found described in the literature are the amides of zinc, sodium, lithium, rubidium, caesium, calcium, barium and strontium, the imide of lithium and a considerable number of metallic nitrides.

8. Ammono Salts.—The obvious parallelism between water and its derivatives, the acids, bases and salts, on the one hand, and ammonia with its family of derivatives, the metallic amides, the acid amides and the ammono salts, on the other, led the writer, collaborating with O. F. Stafford, to study in some detail the reactions between the acid and basic amides in solu-

tion in liquid ammonia.[1] The result of these studies was to show that the acid amides, which discharge the red color of an alkaline solution of phenolphthalein in liquid ammonia, react with soluble metallic amides, which give the characteristic red color with the same indicator, to form metallic derivatives of the acid amides in a manner strictly analogous to the familiar formation of salts in aqueous solution by the interaction of the ordinary acids and bases. For example, acetamide and potassium amide react with each other in ammonia solutions to form monopotassium acetamide, a compound which must be called an ammonoacid salt—acid for the reason that it contains a hydrogen atom replaceable by metal—and dipotassium acetamide, a normal salt, in accordance with the equations

$$CH_3CONH_2 + KNH_2 = CH_2CONHK + NH_3$$

and

$$CH_3CONH_2 + 2KNH_2 = CH_3CONK_2 + 2NH_3$$

which are seen to represent reactions which are analogous to the familiar action of acetic acid on potassium hydroxide in aqueous solution. In addition to these two compounds, Franklin and Stafford prepared the sodium salt of acetamide and the potassium salts of a considerable number of other acid amides,[2] among them urea and sulphamide, the ammonia analogues of carbonic and sulphuric acids, respectively. Formulas for some of these salts are given in the tables above.[3] In general, any ammonia derivative containing a negative element or radical may be expected to react with any derivative of ammonia containing a positive element or radical to give a saltlike compound, as represented by the equations

$$MNH_2 + AcNH_2 = MNHAc + NH_3$$
$$2MNH_2 + AcNH_2 = M_2NAc + 2NH_3, \text{ etc.}$$

Stafford and Franklin have also shown that ammono salts may be prepared by the action of ammonia solutions of ammono acids on certain metals. For example, acetamide in solution

[1] THIS JOURNAL, **28**, 83 (1902).
[2] *Loc. cit.*
[3] P. 294.

in liquid ammonia reacts upon metallic sodium in accordance with the equations

$$CH_3CONH_2 + Na = CH_3CONHNa + H$$
$$CH_3CONHNa + Na = CH_3CONNa_2 + H$$

and upon metallic magnesium in a manner represented by the equation

$$2CH_3CONH_2 + 4NH_3 + Mg = (CH_3CONH)_2Mg.4NH_3 + 2H$$

which, as will be readily recognized, are equations which are strictly analogous to those representing the action of acetic acid on metallic sodium and magnesium, respectively.

Magnesium benzenesulphonamide, $(C_6H_5SO_2NH)_2Mg$, and magnesium cyanoamide, CNNMg, were similarly prepared by the action of liquid ammonia solutions of the acid amides upon the metal.

Some of the ammono salts prepared by Franklin and Stafford are readily soluble in liquid ammonia, others are but slightly soluble or insoluble. Certain of them separate from solution with ammonia of crystallization. They are hydrolyzed completely in the presence of water. Their solutions in liquid ammonia are probably good conductors of electricity, although, unfortunately, this has been proved experimentally for but one representative of the class. Liquid ammonia solutions of mercuric succinimide are excellent conductors.[1]

The soluble members of the class of ammono salts should also enter into metathetic reactions in liquid ammonia solutions, giving precipitates of insoluble ammono salts when the necessary metallic ion is added to their solutions. A solution of potassium acetamide, when added to a solution of silver iodide, for example, may be expected to give a precipitate of an ammonoacetate of silver. Unfortunately, however, such reactions have not yet been studied quantitatively.

A considerable number of metallic derivatives of the acid amides, that is to say, compounds belonging to the class of ammono salts, have been prepared in the past and are found described in the literature. It will be sufficient for our purpose to call attention to a few representative compounds.

[1] J. Am. Chem. Soc., **27**, 196 (1905).

Gal[1] has prepared the zinc salts of acetamide, butyramide, benzamide, carbamide and oxamide by the action of zinc amide, an ammono base, on the respective acid amides in ethereal solution, and Titherley[2] has obtained the sodium derivatives of formamide, acetamide, propionamide and benzamide by the continued action of hot benzene solutions of the acid amides on sodium amide.[2] The reactions whereby these products have been obtained are identical with those studied by Franklin and Stafford, excepting that the former were carried on in solvents other than liquid ammonia. Gal's and Titherly's compounds, like those prepared by Franklin and Stafford, are completely hydrolyzed in the presence of water.

Salts of the stronger ammono acids, that is to say, the metallic derivatives of acid amides containing stronger electronegative groups, are capable of resisting the hydrolytic action of water to a greater or less extent, which accounts for the fact that a considerable number of such compounds—as, for example, the potassium and sodium salts of succinimide, phthalimide, saccharin, the nitrobenzenesulphonamides and the nitroamines,[3] nitrourea,[4] nitrourethane,[4] nitroguanidine,[4] benzenesulphonnitroamide,[5] etc.—have been prepared in the past from aqueous and alcoholic solutions.

The mercury and silver salts of the acid amides show a much greater resistance to the hydrolyzing action of water than do the ammono salts of other metals. Mercuric ammono salts, especially, are unique in this respect. Mercuric acetamide, for example, is so very stable in the presence of water that even aqueous potassium hydroxide fails to effect its hydrolysis.

The metallic derivatives of the acid amides and imides have just been discussed at some length as members of the large class of ammono salts. The fact has not been forgotten, however, that the acid amides of oxygen acids are tautomeric substances;[6] that is to say, they are compounds which

[1] Bull. soc. chim., **39**, 647 (1883).
[2] J. Chem. Soc., **71**, 461 (1897).
[3] Franchimont: Rec. trav. chim., **13**, 308 (1894).
[4] Thiele and Lachman: Ann. Chem. (Liebig), **288**, 267 (1895).
[5] Hinsberg: Ber. d. chem. Ges., **25**, 1093 (1892).
[6] Hantzsch: *Ibid.*, **34**, 3142 (1901).

behave sometimes in accordance with the one, and at other times in accordance with the other, of the two formulas, R-$CONH_2$ and R-CNHOH. The first formula represents the acid amide as an ammono acid, the second as a mixed aquo ammono acid. It may therefore well be that certain metallic derivatives of the acid amides, for example acetamide mercury, are true ammono salts, whereas others, as potassium acetamide, are aquo salts. Certainly, however, in such a compound as dipotassium acetamide, one of the potassium atoms must be in combination with the nitrogen, and is therefore to that extent, at least, an ammono salt. Similarly, the metallic salts of other of the acid amides and imides mentioned above may be the tautomers of the true ammono salts. Potassium succinimide, for example, may be given the formula $\begin{matrix}CH_2CO\\|\\CH_2—C\end{matrix}\!\!>\!\!N\!\!-\!\!OK$ instead of $\begin{matrix}CH_2CO\\|\\CH_2CO\end{matrix}\!\!>\!\!NK$; and potassium methylnitroamine, the formula CH_3-N:NOOK instead of CH_3-NK-NO_2.

However all this may be, no such possibilities exist in connection with the metallic derivatives of the oxygen-free amides. In such compounds as silver cyanoamide, CNNHAg, potassium methylcyanoamide, $CNN(CH_3)K$, potassium succinimidine, $\begin{matrix}CH_2—C(NH)\\|\\CH_2—C(NH)\end{matrix}\!\!>\!\!NK$, etc., there can of course be no question of the manner in which the metal is combined.

A considerable number of compounds belonging to the class of ammono salts are probably to be prepared by the action of potassium amide or of metallic potassium upon the nonmetallic amides and imides, and perhaps even by the action of potassium amide upon the nonmetallic nitrides. The only compound of this kind yet obtained is a potassium ammonotitanate, of the formula N≡Ti-NHK, which has been prepared in the chemical laboratory at Stanford University by Mr. T. B. Hine[1] by the action of potassium amide in excess on titanium bromide. The reaction is represented by the equation

$$TiBr_4 + 5KNH_2 = N{\equiv}Ti\text{-}NHK + 4KBr + 3NH_3$$

[1] Experimental results as yet unpublished.

9. Ammono Salts Analogous to the Zincates, Aluminates, Plumbites, Etc.—Among the phenomena with which the student of chemistry early becomes familiar is the solubility of certain metallic hydroxides, such as the hydroxides of aluminium, lead and zinc, in solutions of the alkali hydroxides, and he soon learns to write confidently the equations

$$Al(OH)_3 + 3KOH = Al(OK)_3 + 3H_2O$$
$$Zn(OH)_2 + 2KOH = Zn(OK)_2 + 2H_2O$$
$$Pb(OH)_2 + 2KOH = Pb(OK)_2 + 2H_2O$$

as representing the reactions which take place. As a matter of fact, the composition of the compounds thus formed is still a matter of doubt.[1]

The observations that certain metallic salts in solution in liquid ammonia, when treated with potassium amide, give precipitates which redissolve on adding the precipitant in excess, suggested the possibility of preparing the ammonia analogues of the substances supposed to be present in the alkaline solutions mentioned above. The results of work in this direction have been highly satisfactory; for most of the compounds so far obtained are beautifully crystalline and of sharply definite composition; results which are in striking contrast to the properties of the analogous oxygen compounds in this respect.

After the earlier unsatisfactory attempts to prepare a potassium ammonoplumbite,[2] the first representative of this class of compounds to be obtained, namely, potassium ammonozincate, was successfully prepared by F. F. Fitzgerald.[3]

Potassium Ammonozincate, $Zn(NHK)_2.2NH_3$.—In view of the fact that metallic zinc dissolves in aqueous potassium hydroxide with the evolution of hydrogen, it was hoped that analogously a pure solution of potassium ammonozincate would be formed by the action of a liquid ammonia solution of potassium amide on the metal. Fitzgerald found that the reaction represented by the equation

$$Zn + 2KNH_2 = Zn(NHK)_2 + H_2$$

[1] Hantzsch: Z. anorg. Chem., **30**, 289 (1902). Wood: J. Chem. Soc., **97**, 878 (1910).

[2] Franklin: J. Am. Chem. Soc., **27**, 843 (1905).

[3] J. Am. Chem. Soc., **29**, 660 (1907). Franklin: *Ibid.*, **29**, 1274 (1907).

takes place readily enough, especially if the zinc is alloyed with a little platinum. Because, however, of the slight solubility of the salt in liquid ammonia, its separation from the excess of zinc is a matter of considerable difficulty.

A second method by which potassium ammonozincate has been successfully prepared[1] is by treating zinc amide, obtained by the action of ammonia gas on zinc ethyl, with a liquid ammonia solution of potassium amide. The amorphous, insoluble zinc amide formed by the action of ammonia on zinc ethyl is converted into a mass of well crystallized potassium salt when allowed to stand overnight in contact with an excess of a solution of potassium amide. The reactions involved are represented by the equations

$$Zn(C_2H_5)_2 + 2NH_3 = Zn(NH_2)_2 + 2C_2H_6$$

and

$$Zn(NH_2)_2 + 2KNH_2 = Zn(NHK)_2.2NH_3$$

Finally, and most conveniently, the salt has been prepared by the action of an excess of potassium amide in solution in liquid ammonia directly upon ammonated zinc iodide, as represented by the equation

$$ZnI_2.4NH_3 + 4KNH_2 = Zn(NH_2)_2.2KNH_2 + 2KI + 4NH_3$$

The crop of well crystallized, slightly soluble zincate thus formed is easily obtained pure by washing with liquid ammonia to remove the potassium iodide formed, together with the excess of potassium amide. Potassium ammonozincate dissolves readily in liquid ammonia solutions of ammonium nitrate.[2] It is energetically hydrolyzed by the action of water; even short exposure to the action of the moisture of the atmosphere produces a superficial sticky layer on the clear, dry crystals. It is not explosive. When heated *in vacuo* potassium ammonozincate remains intact up to 160°; as the temperature is increased beyond this point, the substance melts and gives off ammonia. Heating the salt for some hours at temperatures between 250° and 300° gave a

[1] Fitzgerald: *Loc. cit.*

[2] That is to say, in nitric acid.

residue of approximately the composition represented by the formula $Zn(NHK)_2.{}^1/_2NH_3$.

Potassium Ammonostannate, $Sn(NK)_2.4NH_3$ and $Sn(NK)_2.NH_3$.—The preparation of a pure crystalline salt of the composition represented by the first formula was accomplished by Fitzgerald[1] by the action of potassium amide in excess on a liquid ammonia solution of stannic iodide. The reaction takes place in accordance with the equation

$$SnI_4{}^2 + 6KNH_2 = Sn(NK)_2.4NH_3 + 4KI$$

and since the salt formed is crystalline and but slightly soluble in ammonia, it is easily washed free from potassium iodide and excess of potassium amide. Potassium ammonostannate is soluble in liquid ammonia solutions of ammonium iodide, that is to say, it is decomposed and dissolved by hydriodic acid in liquid ammonia solution. It is vigorously attacked and decomposed by water. Heated in contact with the air it takes fire and burns with brilliant incandescence. It is not explosive. When heated *in vacuo* it loses three molecules of ammonia and is converted into a brick-red powder of the composition represented by the formula $Sn(NK)_2.NH_3$.

It is most interesting to point out the analogies between these two ammono compounds and the corresponding oxygen salts. A formula for potassium metastannate cannot be given corresponding to the formula $Sn(NK)_2.4NH_3$, but if the nitrogen compound be given any one of the formulas $(NH_2)_2:Sn:(NHK)_2.2NH_3$, $(KNH)_2:Sn:(NHNH_4)_2$, or $Sn(NH_2)_4.2KNH_2$, then it is easy to write the analogous formulas, $(HO)_2:Sn:(OK)_2.2H_2O$, $(KO)_2:Sn:(OH_3O)_2$ and $Sn(OH)_4.2KOH$,[3] for the oxygen compound. If Bellucci's contention that the formula for the ordinary trihydrate of potassium metastannate is to be written $K_2Sn(OH)_6$, then analogously the formula for the ammonostannate may be written $K_2Sn(NH_2)_6$. Corresponding to the formula, $K_2SnO_3.3H_2O$, usually given to the aquo salt, the formula $K_2Sn(NH)_3.3NH_3$ may be written for the ammono salt.

[1] J. Am. Chem. Soc., **29**, 1694 (1907).

[2] Stannic iodide forms a white addition product with ammonia.

[3] Cf. Bellucci and Parravano: Z. anorg. Chem., **45**, 142 (1905).

The similarity of the behavior of these two compounds when heated is also noteworthy, for just as the aquo salt loses three molecules of water, so the ammono salt loses three molecules of ammonia, to form compounds which in the one case may be given either of the formulas K_2SnO_3 or $O:Sn:(OK)_2$, and in the other any one of the three formulas $K_2Sn(NH)_3$, $NH:Sn:(NHK)_2$, or $Sn(NK)_2.NH_3$.[1]

Potassium Ammonocadmiate, $Cd(NHK)_2.2NH_3$.[2]—When a solution of potassium amide is added to ammonated cadmium iodide or nitrate, an amorphous or microcrystalline, insoluble product is obtained which analysis shows to be a cadmium salt corresponding in composition to the zinc salt described above.[3]

Potassium Ammonoplumbite, $PbNK.2^1/_2NH_3$, $PbNK.2NH_3$ and $PbNK.NH_3$.—The attempts mentioned above to isolate the product of the action of potassium amide on lead imide have recently been renewed in this laboratory[4] and with entire success. It has been shown that the reaction between the ammono base and the amphoteric imide is to be represented by the equation

$$PbNH + KNH_2 = PbNK + NH_3$$

The salt possesses conspicuous crystallizing power and is obtained from very concentrated solutions in the form of beautifully developed, colorless, transparent crystals, having the composition represented by the formula $PbNK.2^1/_2NH_3$. At 40° below zero, if the pressure is sufficiently low, the salt effloresces, losing one-half a molecule of its ammonia. At 60° it loses an additional molecule of ammonia and is converted into a dark brown mass still showing the form of the original crystals. The product thus formed, $PbNK.NH_3$, does not further lose ammonia when heated to a temperature of 140°. At somewhat higher temperatures the compound explodes.

[1] Howe: J. Am. Chem. Soc., **31**, 259 (1909) first called attention to the remarkable analogies between these aquostannates and ammonostannates.

[2] Prepared in the laboratory of Stanford University by G. S. Bohart. Results not yet published.

[3] It is interesting to note in this connection that cadmium hydroxide has not been observed to possess amphoteric properties.

[4] J. Phys. Chem., **15**, 509 (1911).

It also explodes violently when brought into contact with water or dilute acids, and occasionally even on simple exposure to the atmosphere.

When a solution of ammonium iodide in liquid ammonia is gradually added to a solution of potassium ammonoplumbite, a brown precipitate of lead imide is first formed, which with further addition of ammonium iodide is converted into a white ammonobasic[1] lead iodide. On adding still further quantities of ammonium iodide, the basic lead salt dissolves to form lead iodide. The equations representing these reactions are as follows:

$$PbNK + NH_4I = PbNH + KI + NH_3$$
$$2PbNH + NH_4I = NH_2PbNHPbI.NH_3$$

and

$$PbNPbI.2NH_3 + 3NH_4I = PbI_2 + 6NH_3$$

Conversely, the gradual addition of potassium amide to a solution of lead iodide brings about the successive formation of ammonobasic lead iodide, lead imide and potassium ammonoplumbite.

The analogy between these reactions and those which result from the gradual addition of nitric acid to a solution of potassium plumbite and the inverse reactions which accompany the gradual addition of potassium hydroxide solution to a solution of lead nitrate are so obvious as to require no statement in detail.

Potassium Ammonocuprite, $CuNK_2.2^1/_2NH_3$ and $CuNK_2.NH_3$.—When cuprous nitride, obtained in the manner described by Fitzgerald,[2] is treated with a liquid ammonia solution of potassium amide, a salt of the composition represented by the first of the above formulas is formed, which, because of its extreme solubility, has so far been obtained only in an approximate degree of purity.[3] At low temperatures the salt separates from very concentrated solutions in the form of colorless crystals, which readily part with one and one-half molecules of their ammonia of crystallization. One mole-

[1] *Vide infra*, p. 312: Ammonobasic Salts and Ammonolysis.
[2] *Loc. cit.*
[3] Experimental results not published.

cule of ammonia is retained up to 200°, above which temperature the heating has not been carried.

The formation of potassium ammonocuprite is represented by the equation

$$Cu_3N + 6KNH_2 = 3CuNK_2 + 4NH_3$$

Potassium Ammonothallate, $TlNK_2.4NH_3$, $TlNK_2.2NH_3$ and $TlNK_2.1^1/_3NH_3$.—Black thallium nitride dissolves in liquid ammonia solutions of potassium amide to form a clear, yellow solution from which, on cooling the not too dilute solution, a crop of beautiful, yellow crystals separates. Dried *in vacuo* at —40°, these crystals retain their color and have been shown to have the composition represented by the formula $TlNK_2.4NH_3$ or $TlNH_2.2KNH_2.2NH_3$.[1] On warming up to laboratory temperature the salt takes on a lighter color, loses two molecules of ammonia and is converted into a compound which is represented by the formula $TlNK_2.2NH_3$ or $TlNH_2.2KNH_2$. When heated to 100° the latter compound loses $^2/_9$ of its nitrogen in the form of ammonia and is converted into a black mass to which the formula $TlNK_2.1^1/_3NH_3$ may be given, but which may be merely a mixture of thallium nitride and potassium amide in the proportions represented by the formula $Tl_3N.6KNH_2$. When dry, that is, when free from liquid ammonia, any one of these products explodes with violence on the slightest provocation. The yellow solution of potassium ammonothallate, when treated with a solution of ammonium nitrate, gives first a precipitate of thallium nitride, which then, on further addition of the acid, goes into solution as thallium nitrate.

10. *Ammonobasic Salts. Ammonolysis.*—As has already been shown, the reactions between ammonia and the nonmetallic compounds indicated in the equations given above[2] are strictly analogous to those which take place when the respective substances are treated with water, and are therefore appropriately designated as ammonolytic in order to recall their close relationship to hydrolytic reactions. These particular ammonolytic reactions proceed energetically to com-

[1] Experimental results not yet published.
[2] P. 298.

pletion and are quite as irreversible as are the corresponding reactions which result from the treatment of the halogen compounds of the nonmetals and water. Silicon chloride and the phosphorus chlorides, for example, are completely ammonolyzed in contact with ammonia, just as they are completely hydrolyzed by the action of water. However, just as certain well known hydrolytic reactions are reversible, so also have salts of a number of the less positive metals, when treated with liquid ammonia, been found to give basic precipitates which are increased in amount by the addition of potassium amide, and which are completely dissolved by the addition of an appropriate acid, that is to say, by the addition of an ammonium salt.

Attention was first called to the existence of such reactions by Franklin and Cady[1] who observed the formation of what they assumed to be a "basic bismuth nitrate"[2] around a bismuth anode during the passage of an electric current through a dilute solution of ammonium nitrate in liquid ammonia.

Franklin and Kraus[3] had earlier observed the separation of a small quantity of an insoluble compound accompanying the action of liquid ammonia on mercuric chloride. It was later shown[4] that the formation of this residue is due to the ammonolytic action of liquid ammonia on mercuric chloride, as represented by the equation

$$HgCl_2 + 2NH_3 \rightleftharpoons NH_2HgCl + NH_4Cl$$

and that the product is identical with the well known infusible white precipitate. The reversibility of the reaction is shown by the observation that addition of ammonium chloride to the mercuric chloride prevents the formation of the white precipitate when the mixture is treated with liquid ammonia, and by the fact that addition of sodium amide to the system represented by the above equation displaces the equilibrium to the right, while addition of ammonium chloride solution to the liquid in contact with the precipitate determines the disappearance of the latter.

[1] J. Am. Chem. Soc., **26**, 512 (1904).
[2] "A salt related to ammonia as the ordinary basic nitrate is related to water."
[3] THIS JOURNAL, **23**, 299 (1900).
[4] Franklin: J. Am. Chem. Soc., **27**, 841 (1905).

In an entirely similar manner, lead nitrate, lead iodide, mercuric iodide, mercuric bromide, bismuth iodide, bismuth bromide and stannic iodide undergo ammonolysis to a greater or less extent when treated with liquid ammonia. Although abundantly soluble in liquid ammonia no one of those salts dissolves to a clear solution unless a quantity of an appropriate ammonium salt is present.

The observations of Fitzgerald[1] on the behavior of stannic iodide in solution in liquid ammonia are especially illuminating in this connection. When a limited quantity of liquid ammonia is brought into contact with stannic iodide to which a minute quantity of ammonium iodide has been added, the tin salt dissolves to form a dense, colorless and clear solution. When additional ammonia is distilled into the tube in such a manner as not to mix its contents, the separation of a white precipitate is observed, occupying a zone between the concentrated solution of the stannic iodide and the freshly distilled ammonia. On shaking the tube and thus mixing its contents, the precipitate disappears. On again distilling ammonia into the tube, the precipitate reappears, to disappear again on shaking the tube. The separation of the precipitate may be observed several times by repeating the operations thus described. After a relatively large amount of liquid ammonia has been added, the precipitate becomes permanent, and the separation of tin from the solution is complete, as is shown by the observation that the addition of potassium amide to the supernatant solution fails to produce any further precipitation. The addition of any considerable quantity of ammonium iodide to the solution in the beginning prevents the ammonolysis of the salt. Whether in this particular instance the product of ammonolysis is an ammonobasic salt, or an amide; imide or nitride of tin, free from iodine, has not been determined. The remarkably close parallelism between the phenomena just described and the familiar action of water on acid solutions of antimony chloride and bismuth chloride is so obvious as to require no further comment.

The ammonobasic salts of definite composition which have

[1] J. Am. Chem. Soc., **29**, 1695 (1907).

so far been obtained are the ammonobasic mercuric halides of the respective formulas NH_2-Hg-Cl, Hg:N-Hg-Br and Hg:N-Hg-I, and the ammonobasic lead iodide of the formula Pb:N-Pb-I.$2NH_3$. The reactions whereby these compounds have been obtained are represented by the equations

$$HgCl_2 + 2NH_3 = NH_2\text{-}Hg\text{-}Cl + NH_4Cl$$
$$2HgBr_2 + 4NH_3 = Hg{:}N\text{-}Hg\text{-}Br + 3NH_4Br$$
$$2HgI_2 + 4NH_3 = Hg{:}N\text{-}Hg.I + 3NH_4I$$
$$2PbI_2 + 6NH_3 = Pb{:}N\text{-}Pb\text{-}I.2NH_3 + 3NH_4I$$

the amount of ammonobasic salt formed being increased to a reasonable yield, when desired, by the addition of limited quantities of potassium amide.

The ammonobasic salts which have thus been obtained as definite chemical compounds, as well as the others described above as having been observed qualitatively, all appear as insoluble, amorphous precipitates,[1] characteristics which, as is well known, attach to the more familiar aquobasic salts. Even the tendency of the latter class of products to form basic mixtures of more or less indefinite composition is exemplified in the failure of attempts[2] to obtain ammonobasic compounds of definite composition from either aluminium or antimony iodide. In the case of antimony iodide it is interesting to note that continued agitation, through several weeks, of the finely divided salt with liquid ammonia—which, as the ammonia abstracted iodine from the salt in the form of ammonium iodide, was from time to time replaced by fresh solvent—failed, in the hands of Fitzgerald, to yield a compound of definite composition.

In addition to the compounds of mercury, two other representatives of the class of ammonobasic salts are found described in the literature. The ammonobasic titanium halides represented by the formulas N≡Ti-Cl and N≡Ti-Br have been prepared by Ruff and Eisner[3] by the action of liquid

[1] In two tubes containing mercuric chloride and liquid ammonia which were sealed up six or eight years ago, the white, apparently amorphous precipitates of NH_2HgCl which separated at that time have changed into aggregates of well developed crystals.

[2] Franklin: J. Am. Chem. Soc., **27**, 849 (1905).

[3] Ber. d. chem. Ges., **41**, 2250 (1908).

ammonia on the chloride and bromide of titanium, respectively.

11. Ammonobasic Mercuric Salts.—The formation of the ammonobasic mercuric salts NH_2-Hg-Cl, Hg:N-Hg-Br and Hg:N-Hg-I by the ammonolysis of mercuric chloride, bromide and iodide, respectively, in liquid ammonia solution are facts which have an important bearing upon the question of the constitution of the large group of the so-called mercuriammonium compounds, a question which has never received a satisfactory answer.

Since these ammonobasic mercuric salts, the preparation and description of which have been given in a previous paper,[1] cannot be distinguished from the respective products of the action of aqua ammonia on the mercuric halides, it follows that the latter compounds are identical with the former. It is therefore altogether wrong to formulate the ammonobasic mercuric chloride, NH_2-Hg-Cl, as a double salt of dimercuriammonium chloride and ammonium chloride, Hg_2N^V-Cl. NH_4Cl, and the ammonobasic iodide, Hg:N-Hg-I, as dimercuriammonium iodide, Hg_2N^V-I, as is done in the majority of the dictionaries and handbooks of chemistry.

In a subsequent paper the attempt will be made to show that all the mercury ammonia compounds described in the literature, instead of being ammonium salts in which ammonium hydrogen is substituted by mercury—as the various mercuriammonium theories assume them to be—are, as a matter of fact, either normal mercuric salts with ammonia of crystallization, or basic products resulting from ammonolysis, or both ammonolysis and hydrolysis, of the normal mercuric salts.

CONCLUSION

It has been shown in this paper that an ammonia system of acids, bases and salts may be formulated on the basis of ammonia as the typical substance, and in a manner entirely analogous to the formulation of the ordinary oxygen acids, bases and salts as derivatives of water. In other words, a system of acids, bases and salts has been developed in which

[1] J. Am. Chem. Soc., 27, 838 (1905).

nitrogen occupies a position similar to that occupied by oxygen in the system of Lavoisier.

The acids of the ammonia system are the acid amides and imides, including the amides and imides of the nonmetallic elements; the bases of the system are the metallic amides and imides; the salts are the metallic derivatives of the acid amides and imides.

In order to emphasize their relations to ammonia, and for convenience in discussing the reactions between representatives of the ammonia system, these acids, bases and salts are referred to as ammono acids, ammono bases and ammono salts, respectively.

Reactions in liquid ammonia solutions which are strictly analogous to the familiar hydrolytic reactions in water solutions have been discovered and are accordingly designated as ammonolytic reactions. Products which have been named ammonobasic salts are shown to result from the ammonolysis of certain salts of the heavy metals.

It is shown in this paper that the relationships indicated by this system of nomenclature are by no means purely formal. The ammono acids exhibit certain truly acid properties, the ammono bases react in liquid ammonia solutions in a manner strictly analogous to the familiar reactions of the ordinary bases in aqueous solutions, and the ammono salts are as certainly saltlike compounds as are the products of the interaction of ordinary acids and bases.

A considerable number of new representatives of the ammonia system of acids, bases and salts have been made by means of reactions carried on in liquid ammonia solutions and are found described in the above pages.

CHEMICAL DIVISION
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A FURTHER STUDY OF TWO OF THE PRODUCTS OF THE TRANSFORMATION OF PARASULPHAMIDOBENZOIC ACID WHEN HEATED TO 220°[1]

By J. S. Chamberlain

The results obtained by Stoddard[2] led to the conclusion that the acid which Muckenfuss had called "iso-parasulphaminebenzoic acid" is not isomeric with *p*-sulphamidobenzoic acid, but is the anhydride, corresponding to the anhydride of *o*-sulphamidobenzoic acid, or benzoic sulphinide, $C_6H_4\begin{cases}CO\\SO_2\end{cases}NH$. Stoddard also showed that when the "infusible diamide" is boiled with magnesium hydroxide, it loses half of its nitrogen and yields a salt of an acid isomeric with *p*-sulphamidobenzoic acid—probably *p*-carbamidobenzenesulphonic acid, $C_6H_4\begin{cases}CONH_2\\SO_2OH\ (p)\end{cases}$.

It was in the hope of securing further evidence in regard to these two points that the work described in this article was taken up at the suggestion of Professor Remsen.

The heating of the carefully purified *p*-sulphamidobenzoic acid was carried out in large test tubes which were sealed after being filled. It was found that by using this method but little charring took place.

As noticed by Muckenfuss[3] and by Stoddard,[4] a crystalline sublimate is always formed during the melting. This was collected from all the tubes in which the melting was carried out and was found to be *p*-sulphamidobenzoic acid.

Under the most favorable conditions the fused product, obtained by heating the *p*-sulphamidobenzoic acid for eight hours at 220°, is of a light brown color and consists of four substances isolated by Muckenfuss.[4] When this product is powdered and extracted with boiling alcohol, a flocculent

[1] See Note, This Journal, **47**, 1.
[2] *Ibid.*, **47**, 1.
[3] *Ibid.*, **18**, 349.
[4] *Loc. cit.*

mass of fine needlelike crystals is deposited from the filtrate on cooling. These crystals are entirely distinct from the thick prismatic crystals of acid ammonium *p*-sulphobenzoate extracted at the same time; this latter is more soluble in alcohol, and remains in solution until the extract is evaporated to a quite concentrated condition. The fine needle crystals first obtained are of neutral reaction and yield ammonia readily in the cold when treated with sodium hydroxide. On adding barium chloride to a solution of the crystals the well-characterized barium salt is obtained.

The Ammonium Salt of p-*Benzoic Sulphinide.*—The fine needle crystals obtained as the first product from the alcoholic extract were purified by recrystallizing three times from hot alcohol. It was found that while ordinarily, as thrown down from a somewhat concentrated alcoholic solution, the crystals were distinctly needle-shaped, yet, when filtered off and redissolved in alcohol or water and allowed to crystallize slowly from a dilute solution, they were in the form of minute glistening plates that gave to the mass in the liquid a characteristic micaceous appearance. The crystals probably always form as plates, but when they separate from a concentrated solution the plates are very small and arrange themselves in rows and thus have the appearance of needles.

The salt is very soluble in water but less so in alcohol. It probably contains no water of crystallization, as a loss equal to only one-half molecule of water was obtained on drying. It gives up one-half of its nitrogen as ammonia on boiling with magnesium hydroxide and does not give up any more with sodium hydroxide.

The analyses of the ammonium salt that had been recrystallized gave the following results:

0.4194 gram salt gave at 300° 0.0198 gram H_2O.
0.0506 gram salt gave 0.0629 gram $BaSO_4$ (Carius).
0.0944 gram salt gave 0.1190 gram $BaSO_4$ (Carius).
0.0920 gram salt gave 0.1148 gram $BaSO_4$ (Carius).
0.0955 gram salt gave 0.01327 gram N (Dumas).
0.1368 gram salt gave 0.01779 gram N (Dumas).
0.2069 gram salt gave 0.0143 gram N (by NaOH).
0.1166 gram salt gave 0.00858 gram N (by NaOH).
0.1846 gram salt gave 0.01173 gram N (by NaOH).

	Calculated for $C_6H_4\langle^{CO}_{SO_2}\rangle N.NH_4$	Calculated for $C_6H_4\langle^{CONH_2}_{SO_2ONH_4}$	Found		
$^1/_2$ H_2O	4.3	4.0	...	4.72	...
S	16.0	14.68	17.06	17.31	17.13
N (total)	14.0	12.84	13.90	13.00	...
N (one-half)	7.0	6.42	6.91	7.36	6.35

The results of these analyses indicate that the salt cannot be purified by recrystallization. The difficulty comes probably from the fact that there is present with the ammonium salt some of the acid ammonium *p*-sulphobenzoate that is extracted by the alcohol at the same time and that is not removed by recrystallization. An attempt was made to purify the salt by dissolving in water and then adding acetone, but the method did not work well.

The preceding results, while not as good as could be desired, show that the original crystals obtained from the alcoholic extract of the fused product are the ammonium salt and not the free acid. It was then desirable to see if an ammonium salt prepared from the barium salt would be the same as the one just studied. In order to test this point, the barium salt, prepared as described below and the purity of which had been tested by analysis, was dissolved in water and ammonium sulphate added in slightly less quantity that was required to precipitate all of the barium. The barium sulphate was then filtered off and the filtrate evaporated. The residue was extracted with alcohol and the crystals separating out were recrystallized. The substance thus obtained resembled in all respects the salt originally obtained from the alcoholic extract of the fused product. In the last analyses the ammonium salt was prepared by using an excess of ammonium carbonate to precipitate the barium and then driving off the excess of ammonium carbonate from the filtrate by boiling.

0.0172 gram salt gave at 300° 0.0078 gram H_2O.
0.0491 gram salt gave 0.00347 gram N (by NaOH).
0.0983 gram salt gave 0.0158 gram N (Dumas).
0.0108 gram salt gave 0.0130 gram $BaSO_4$ (Carius).
0.0655 gram salt gave 0.0763 gram $BaSO_4$ (Carius).

	Calculated for $C_6H_4\langle^{CO}_{SO_2}\rangle N.NH_4$	Calculated for $C_6H_4\langle^{CONH_2}_{SO_2ONH_4}$	Found
$^1/_2$ H_2O	4.3	4.0	4.53
S	16.0	14.68	16.52, 15.99
N (total)	14.0	12.84	16.07
N (one-half)	7.0	6.42	7.06

The Barium Salt.—The crystals of the ammonium salt, as they are deposited from the alcoholic extract, were dissolved in water and barium chloride added. The characteristic barium salt was precipitated in fine needles forming a thick, gelatinous mass. The purification of this salt was accomplished by recrystallizing from hot water. It was difficult to secure samples that seemed pure as indicated by analysis. The reason for this is probably the same as that stated before in connection with the purification of the ammonium salt, that is, the presence in the original extract of a little acid ammonium *p*-sulphobenzoate. Several other methods of purification were tried but none worked as well as simple recrystallization. The number of recrystallizations made was as high as nine, when the final products gave fairly concordant results.

The character of the salt is such that proper drying for determination of the water of crystallization is exceedingly difficult. The crystals are so fine it is impossible to dry them at once by means of absorbent paper and the salt loses water so readily that quick drying is absolutely necessary for correct determinations. For this reason, the determinations of water of crystallization vary a great deal and little reliability can be placed upon them. The first three determinations were made with salt that was dried first on a porous plate until dry enough not to stick to absorbent paper and then pressed between folds of paper until reduced to a fine powder. In the third determination the pressing between papers was not so long as in the other cases. In the fourth the salt was allowed to remain for a long time on a porous plate in the air. The results obtained are as follows:

I. 0.0984 gram salt lost at 220° 0.009 gram H_2O.
II. 0.050 gram salt lost at 220° 0.0048 gram H_2O.

III. 0.0691 gram salt lost at 220° 0.0075 gram H_2O.
IV. 3.2630 gram salt lost at 220° 0.1645 gram H_2O.

Calculated for $\left(C_6H_4\begin{smallmatrix}CO\\SO_2\end{smallmatrix}N\right)_2Ba + 3H_2O$	Found I	II	III	IV
9.73	9.14	9.60	10.85	5.04

In the estimations recorded below the anhydrous salt was used.

First Series

Sample

I. 0.1655 gram salt gave 0.0768 gram $BaSO_4$.
II. 0.2253 gram salt gave 0.1044 gram $BaSO_4$.
II. 0.2379 gram salt gave 0.1097 gram $BaSO_4$.
II. 0.1551 gram salt gave 0.0718 gram $BaSO_4$.
II. 0.1278 gram salt gave 0.0592 gram $BaSO_4$.
III. 0.1577 gram salt gave 0.0725 gram $BaSO_4$.

Second Series

Recrystallization

2 0.1068 gram salt gave 0.0473 gram $BaSO_4$.
3 0.1282 gram salt gave 0.0583 gram $BaSO_4$.
4 0.1680 gram salt gave 0.0771 gram $BaSO_4$.
5 0.0884 gram salt gave 0.0400 gram $BaSO_4$
6 0.0560 gram salt gave 0.0257 gram $BaSO_4$.
7 0.0758 gram salt gave 0.0350 gram $BaSO_4$.
8 0.1917 gram salt gave 0.0887 gram $BaSO_4$.
9 0.1074 gram alt gave 0.0500 gram $BaSO_4$.
9 0.1159 gram salt gave 0.0538 gram $BaSO_4$.

Third Series

5 0.0669 gram salt gave 0.0298 gram $BaSO_4$.
5 0.0585 gram salt gave 0.0260 gram $BaSO_4$.
6 0.0535 gram salt gave 0.0241 gram $BaSO_4$.
8 0.1261 gram salt gave 0.0576 gram $BaSO_4$.
9 0.0942 gram salt gave 0.0431 gram $BaSO_4$.
9 0.0628 gram salt gave 0.0288 gram $BaSO_4$.
9 (by alcohol) 0.1618 gram salt gave 0.0740 gram $BaSO_4$.
9 (by alcohol) 0.1081 gram salt gave 0.0495 gram $BaSO_4$.

0.2142 gram salt gave 0.0121 gram N (Dumas).
0.1369 gram salt gave 0.0082 gram N (Dumas).
0.2952 gram salt gave 0.01679 gram N (Dumas).

0.1301 gram salt gave 0.1193 gram $BaSO_4$ (Carius).
0.1455 gram salt gave 0.1382 gram $BaSO_4$ (Carius).
0.1311 gram salt gave 0.1230 gram $BaSO_4$ (Carius).
0.0898 gram salt gave 0.0867 gram $BaSO_4$ (Carius).

		Ba	S	N
Calculated for $\left(C_6H_4\begin{smallmatrix}CO\\SO_2\end{smallmatrix}N\right)_2Ba$		27.34	12.77	5.59
Calculated for $\left(C_6H_4\begin{smallmatrix}CONH_2\\SO_2O\end{smallmatrix}\right)_2Ba$		25.51	11.91	5.21
Found	Sample			
First Series	I	27.25	...	...
	II	27.24	12.59	5.63
	II	27.11	13.03	..
	II	27.22	12.88	5.98
	II	27.24	...	5.68
	III	27.03	13.25	..
	Recrystallization			
Second Series	2	26.04		
	3	26.74		
	4	26.98		
	5	26.60		
	6	27.00		
	7	27.15		
	8	27.20		
	9	27.37		
	9	27.29		
Third Series	5	26.19		
	5	26.15		
	6	26.48		
	8	26.85		
	9	26.90		
	9	26.96		
	9 (by alcohol)	26.89		
	9 (by alcohol)	26.92		

These results would seem to leave no room for doubt that the acid from which this salt is derived is in reality *p*-benzoic sulphinide.

Copper Salt.—When copper sulphate is added to a solution of the barium salt, in slightly less quantity than required to precipitate all of the barium, and the barium sulphate is filtered off, the filtrate, when evaporated nearly to dryness, yields small bunches of blue crystals. On removing the crystals from the viscous mother liquor they become pasty and on drying cake up into hard masses. The salt was dried at 150° before being analyzed.

0.1022 gram salt gave 0.0191 gram CuO.

	Calculated for $\left(C_6H_4\begin{smallmatrix}CO\\SO_2\end{smallmatrix}N\right)_2Cu$	Found
Cu	14.75	14.80

Lead Salt.—The lead salt was made from the free sulphinide, prepared by precipitating all of the barium from a solution of the barium salt by means of sulphuric acid. A solution of the free sulphinide, thus obtained, was boiled with lead carbonate and the excess of carbonate filtered off. On evaporating the filtrate, crystals separated but were so indistinct that it was impossible to make out their form. They did not become pasty and cake up in hard masses like the copper salt. The salt was analyzed for water and for lead.

0.0768 gram salt gave at 170° 0.0067 gram H_2O.
0.0697 gram salt gave at 170° 0.0333 gram $PbSO_4$.
0.0791 gram salt gave at 170° 0.0377 gram $PbSO_4$.

	Calculated for $\left(C_6H_4\begin{smallmatrix}CO\\SO_2\end{smallmatrix}N\right)_2Pb + 3H_2O$	Found
$3H_2O$	8.67	8.72
Pb	36.24	35.74, 34.37

From the results of the analyses, especially those of the barium and ammonium salts, when we consider the character of the salts, which renders their preparation in a pure form for analysis very difficult, it seems very probable, to say the least, that they are derived from *p*-benzoic sulphinide,

$$p\text{-}C_6H_4\begin{smallmatrix}CO\\SO_2\end{smallmatrix}NH$$

analogous to *o*-benzoic sulphinide.

"Infusible Diamide"

After the fusion product, obtained by heating *p*-sulphamidobenzoic acid to 220°, had been extracted with alcohol and all of the ammonium *p*-benzoic sulphinide removed, the residue was shaken thoroughly with a small quantity of cold water. This removed all traces of ammonium *p*-benzoic sulphinide, and also acid ammonium *p*-sulphobenzoate. The

residue, after filtration, was dissolved in cold, dilute sodium hydroxide and decolorized by means of animal charcoal. After filtering off the charcoal the "diamide" was precipitated from the clear liquid by addition of hydrochloric acid. The "diamide" thus obtained was pure white and, when thrown down slowly from a somewhat dilute solution, the crystals were in the form of thin, almost square, plates. If, however, crystallization took place suddenly, from a concentrated solution, the plates evidently arranged themselves in rows and appeared as needles. This same peculiarity of crystallization was noticed in the case of the ammonium *p*-benzoic sulphinide. The identity of the two crystal forms of the "diamide" was proved beyond a doubt by repeated transformations of one form into the other.

The pure "diamide" obtained agrees in all respects with that described by Muckenfuss[1] and Stoddard.[2] It is infusible, very slightly soluble in cold water, more soluble in hot water and insoluble in acids and alcohol and other organic solvents. It is readily soluble in sodium hydroxide and barium hydroxide, yielding ammonia even in the cold with magnesium hydroxide and potassium carbonate; it yields one-half of its nitrogen, as ammonia, on boiling with these last two reagents.

In the following analysis of the "diamide," nitrogen was determined by distilling from sodium hydroxide and collecting the ammonia liberated in standard acid solution. The excess of acid was then determined by titration with standard alkali.

0.2631 gram diamide gave 0.03557 gram N.
0.3851 gram diamide gave 0.05502 gram N.
0.2912 gram diamide gave 0.04171 gram N.
0.3298 gram diamide gave 0.04686 gram N.
0.1705 gram diamide gave 0.02467 gram N.

Also by Dumas' method.

0.2641 gram diamide gave 0.03655 gram N.
0.3101 gram diamide gave 0.04324 gram N.

	Calculated for $C_6H_4\langle^{CO}_{SO}(NH_2)_2$	Found
N	14.00	13.48, 14.28, 14.32, 14.21, 14.46
		(Dumas) 13.84, 13.94

[1] This Journal, **18**, 355.
[2] *Loc. cit.*

Stoddard[1] found that when the "infusible diamide" is boiled with magnesium hydroxide, only one-half of the total nitrogen is liberated as ammonia. Determinations of nitrogen by this method gave the following results:

0.4170 gram diamide gave 0.03017 gram N.
0.6553 gram diamide gave 0.04810 gram N.
0.6580 gram diamide gave 0.04845 gram N.
0.4795 gram diamide gave 0.03496 gram N.
1.8825 grams diamide gave 0.13525 gram N.
1.7765 grams diamide gave 0.12709 gram N.
3.4585 grams diamide gave 0.2365 gram N.

	Calculated for $C_6H_4\begin{matrix}CO\\SO_2\end{matrix}(NH_2)_2$	Found
$^1/_2$ N	7.0	7.23, 7.34, 7.36, 7.29 7.18, 7.15, 6.84

These results leave no room for doubt that the "infusible diamide" is isomeric with the ordinary diamide and further, as shown by the action of magnesium hydroxide and later by the action of potassium carbonate, it contains two nitrogen atoms that are evidently not in the same condition.

Magnesium Salt.—When the "infusible diamide" is boiled with magnesium hydroxide there is at first a rapid evolution of ammonia and, as shown by the analyses, the ammonia liberated is equivalent to only one-half of the nitrogen contained in the "diamide." After long-continued boiling only a very little more than the calculated amount of nitrogen could be obtained.

After the ammonia had all been driven off from the solution containing "diamide" and magnesium hydroxide, the excess of magnesium hydroxide was removed by filtration and the filtrate evaporated. From the concentrated solution crystals of the magnesium salt separated that agreed in all respects with those of Stoddard.[1]

The salt crystallizes in small diamond-shaped crystals that are readily soluble in water but insoluble in alcohol or ether. It yields ammonia when warmed with sodium hydroxide but

[1] *Loc. cit.*

not with potassium carbonate. After all the nitrogen had been liberated by sodium hydroxide neutral sodium *p*-sulphobenzoate was formed, as was shown by transformation into the characteristic acid barium salt.

It was found that magnesium could not be determined by direct ignition to the oxide and it was therefore determined by dissolving the salt in water and precipitating the magnesium as magnesium ammonium phosphate and subsequently igniting it to pyrophosphate. The results of the analyses are:

0.3748 gram salt gave 0.0535 gram H_2O.
0.1757 gram salt gave 0.0459 gram $Mg_2P_2O_7$.
0.2230 gram salt gave 0.0570 gram $Mg_2P_2O_7$.
0.2201 gram salt gave 0.01492 gram N (Dumas).
0.0982 gram salt gave 0.1089 gram $BaSO_4$ (Carius).

	Calculated for $\left(C_6H_4\begin{matrix}CO\\SO_2\end{matrix}\left(\begin{matrix}NH_2\\O\end{matrix}\right)\right)_2Mg$	Found
$4H_2O$	14.52	14.27
Mg	5.66	5.64, 5.52
N	6.60	6.78
S	15.09	15.22

Potassium Salt.—On treating a solution of the magnesium salt with potassium carbonate and filtering off the precipitated magnesium carbonate, crystals of the potassium salt, as described by Stoddard,[1] are obtained by evaporating the filtrate.

The potassium salt is very characteristic, forming beautiful, clear, spindle-shaped crystals that remain wholly separate from each other unless the solution is concentrated. They contain no water of crystallization and are readily soluble in water. On warming with sodium hydroxide ammonia is given off just as in the case of the magnesium salt.

0.1192 gram salt gave 0.0426 gram K_2SO_4.
0.2526 gram salt gave 0.0911 gram K_2SO_4.
0.0609 gram salt gave 0.0207 gram K_2SO_4.
0.0505 gram salt gave 0.0180 gram K_2SO_4.
0.2711 gram salt gave 0.01654 gram N (Dumas).
0.0962 gram salt gave 0.0962 gram $BaSO_4$ (Carius).

[1] *Loc. cit.*

	Calculated for $C_6H_4\langle^{CO}_{SO_2}\rangle\binom{NH_2}{OK}$	Found
K	16.32	16.06, 16.20, 16.01, 16.02
N	5.86	6.10
S	13.39	13.73

Action of Potassium Carbonate on the Diamide

Stoddard[1] states that sodium carbonate liberates more than one-half of the nitrogen from the "diamide" on boiling. This appeared strange, in view of the fact that if one-half of the nitrogen is first liberated from the "diamide" by boiling with magnesium hydroxide, a magnesium salt is formed, containing the remaining atom of nitrogen, and this nitrogen is not driven out from the magnesium salt by means of potassium carbonate. If then the nitrogen is all driven out of the "diamide" by potassium carbonate and not at all from the magnesium salt, the one atom of nitrogen in the magnesium salt is evidently in a different condition from that which it occupied in the "diamide." It seemed, therefore, that by boiling the "diamide" with potassium carbonate it should be possible to obtain the same salt that is formed indirectly from the diamide through the magnesium salt. In order to test this point the following experiments were made:

1. One portion of "diamide" was treated with the calculated quantity of potassium carbonate sufficient to replace one atom of nitrogen, and another portion was treated with double this quantity. Both solutions on boiling gave off ammonia and on evaporation deposited crystals. In both cases, however, the crystals that separated were identical and exactly corresponded to those obtained from the magnesium salt. In neither case was any trace of neutral potassium sulphobenzoate observed nor of any other salt than the one mentioned.

2. Two portions of the magnesium salt, prepared from the "diamide" by magnesium hydroxide, were taken. One portion was treated with a quantity of potassium carbonate just sufficient to replace the magnesium and the other with double this quantity. In neither case was there any evidence of

[1] *Loc. cit.*

liberation of ammonia and from both solutions a potassium salt crystallized which was identical with that obtained in the first experiment. The identity of all these salts was corroborated by analysis.

It is thus shown that potassium carbonate does not liberate more than one-half of the nitrogen of the "diamide" and that the nitrogen atom in the magnesium and potassium salts is undoubtedly in the same condition as in the "diamide." The potassium salt, therefore, is obtained much more easily by boiling the diamide directly with potassium carbonate.

Barium Salt.—It was found that when the potassium salt, in solution, was treated with the calculated amount of barium chloride sufficient to replace the potassium, on evaporation of the solution a little, crystals separated out that looked like the potassium salt but they were found to contain barium. They are clear and spindle-shaped, but are less soluble than the potassium salt and are thrown down from a more dilute solution not separate but grouped together in clusters. The salt contains no water of crystallization and gives off ammonia when heated with sodium hydroxide, but not with potassium carbonate. The solution is not precipitated by addition of hydrochloric acid. After ammonia has been driven off by sodium hydroxide, hydrochloric acid precipitates the characteristic acid barium *p*-sulphobenzoate.

0.0397 gram salt gave 0.0173 gram $BaSO_4$.
0.0728 gram salt gave 0.0641 gram $BaSO_4$ (Carius).
0.0991 gram salt gave 0.00583 gram N (Dumas).

	Calculated for $\left(C_6H_4\begin{matrix}CO\\SO_2\end{matrix}\left(\begin{matrix}NH_2\\O\end{matrix}\right)\right)_2Ba$	Found
Ba	25.51	25.62
S	11.91	12.09
N	5.21	5.80

Action of Barium Hydroxide upon the "Diamide"

A portion of the "diamide" was treated with an excess of barium hydroxide and the solution kept cool. In order to carry off the ammonia that was liberated, a current of air, free from carbon dioxide and ammonia, was drawn through

the solution and into a solution of standard sulphuric acid. The action was allowed to continue until approximately the equivalent of one-half of the nitrogen had been set free from the "diamide." The excess of barium hydroxide was then removed from the solution by carbon dioxide and the filtrate evaporated to crystallization. During the evaporation some unchanged "diamide" separated out and also some acid barium *p*-sulphobenzoate. When the solution had been evaporated nearly to dryness a crystalline substance separated, but this proved to be almost pure neutral barium *p*-sulphobenzoate. No evidence of any other crystalline product was found. A striking feature of the experiment, however, was that the concentrated mother liquor, after the neutral barium *p*-sulphobenzoate had crystallized out, seemed to contain a substance rich in nitrogen. On treating the mother liquor with sodium hydroxide there was an abundant evolution of ammonia at once. The ammonia was given off much more easily than from the "diamide" and the quantity seemed much greater than would have been obtained from the quantity of "diamide" that could have been held in solution in the amount of liquid present. All efforts to isolate a new salt from this solution failed.

Barium hydroxide therefore acts like sodium hydroxide and liberates all the nitrogen from the "diamide," forming the neutral *p*-sulphobenzoate, and no intermediate salt containing one atom of nitrogen was obtained in this way. It seems possible that the barium hydroxide may have formed a very soluble salt with the "diamide" without driving out any of the nitrogen.

Preparation of Potassium p-*Carbamidobenzenesulphonate*

Wilson[1] has studied in this laboratory the salts of *o*-carbamidobenzenesulphonic acid. The method used was one obtained from patent literature and consists in heating a mixture of acid potassium *o*-sulphobenzoate and ammonium sulphocyanate.

$$o\text{-}C_6H_4\begin{cases}COOH\\SO_3OK\end{cases} + NH_4CNS = C_6H_4\begin{cases}CONH_2\\SO_3OK\end{cases} + x$$

[1] THIS JOURNAL, **30**, 353.

The same reaction was tried with the para compound, to see if salts of *p*-carbamidobenzenesulphonic acid could be obtained and to compare them with the salts obtained from the "diamide." A quantity of acid potassium *p*-sulphobenzoate was mixed with about twice the theoretical amount of ammonium sulphocyanate and heated for several days, first just to the fusion point, and later to 200°. The product was then powdered and dissolved in water, all but a small amount of sulphurous matter going into solution readily. The solution was decolorized by boiling with animal charcoal and the filtrate evaporated to crystallization. Crystals did not appear until the solution was quite concentrated, when fine short needles or prisms separated which were distinctly different from the clear spindle-shaped crystals obtained from the "diamide" by boiling with potassium carbonate. The crystals come down in masses and are not separate and distinct in form. The salt yields ammonia when heated with sodium hydroxide or barium hydroxide but not with potassium carbonate. It contains no water of crystallization.

0.0859 gram salt gave 0.0306 gram K_2SO_4.
0.0522 gram salt gave 0.0535 gram $BaSO_4$ (Carius).
0.1017 gram salt gave 0.0126 gram N (Dumas).

	Calculated for $C_6H_4\langle^{CONH_2}_{SO_2OK}$	Found
K	16.32	16.01
S	13.39	14.07
N	5.86	12.39

Sodium Salt.—The sodium salt was prepared in exactly the same way. The salt did not crystallize except from a very concentrated solution and the crystals were indistinct, as in the case of the potassium salt. One analysis for sodium was made.

0.0597 gram salt gave 0.0191 gram Na_2SO_4.

	Calculated for $C_6H_4\langle^{CONH_2}_{SO_2ONa}$	Found
Na	10.31	10.37

Silver Salt.—From the sodium salt, the silver salt was prepared by adding to a solution of the salt in water the calculated amount of silver nitrate sufficient to replace the sodium. The silver salt crystallized out in starlike clusters of thin leaves or plates that darken in the light. The crystals were removed, dried quickly with paper and analyzed for silver.

0.0139 gram salt gave 0.0046 gram Ag.

	Calculated for $C_6H_4\langle^{CONH_2}_{SO_2OAg} + H_2O$	Found
Ag	33.13	33.09

Barium Salt.—By adding barium chloride to a solution of the potassium salt it was thought that the barium salt might be formed and crystallize out before the potassium salt, as in the case of the corresponding salts obtained from the "diamide." The barium salt did not crystallize out in anything that looked like a pure form. The salt was certainly not the same as was obtained from the "diamide" through the potassium salt. It gave ammonia with sodium hydroxide and with barium hydroxide.

Further evidence in regard to these salts was not obtained in this study.

Summary

From the results of the analyses of the barium and ammonium salts it seems highly probable that Stoddard[1] was right in giving to the substance, which Muckenfuss[1] had called the "iso-*p*-sulphaminebenzoic acid," the anhydride or sulphinide formula, $p\text{-}C_6H_4\langle^{CO}_{SO_2}\rangle NH$. This is formed, not as the free sulphinide, but as the ammonium salt, when *p*-sulphamidobenzoic acid is heated to 220°.

That the salts are derived from *p*-benzoic sulphinide and not from carbamidosulphonic acid is rendered still more probable by the fact mentioned by Muckenfuss[1] that the barium salt gives off no ammonia on boiling with sodium hydroxide and also by the fact[2] that the ammonium salt gives one-half of its

[1] *Loc. cit.*

[2] See p. 326.

nitrogen as ammonia when heated with magnesium hydroxide, but the remaining atom of nitrogen is not removed even on boiling with sodium hydroxide. While from the data at disposal it seems probable that the substance under consideration is the para analogue of benzoic sulphinide, this is by no means to be regarded as established.

That the salts obtained from the "infusible diamide" still hold in combination one nitrogen atom that is not in the sulphamido grouping is certain and it thus seems very probable that it is in the carbamido grouping and that the salts are true isomers of those of *p*-sulphamidobenzoic acid.

In regard to the salts made by heating acid potassium *p*-sulphobenzoate with ammonium sulphocyanate, further investigation is necessary to establish their composition and constitution.

Little evidence has been obtained bearing upon the constitution of the "infusible diamide." That the two nitrogen atoms are in different conditions appears certain, and yet it is improbable that either one is in the sulphamido condition.

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A STUDY OF THE PRODUCTS FORMED BY THE ACTION OF HEAT ON PARASULPHAMIDOMETATOLUIC ACID

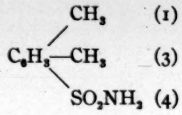
BY C. E. WATERS[1]

The curious results obtained in this laboratory in studying the effect of heat on *p*-sulphamidobenzoic acid led to a desire to learn whether derivatives of this acid conduct themselves in the same way and at the suggestion of Professor Remsen the study of the effect of heat on *p*-sulphamido-*m*-toluic acid was taken up in order to determine whether the presence of a methyl group in the ortho position to the sulphamido group has any influence on the result. It was found, as will be seen later, that changes similar to those that take place in *p*-sulphamidobenzoic acid took place in this case also.

The *p*-sulphamido-*m*-toluic acid used was made according

[1] See Note, THIS JOURNAL, 47, 1.

to the directions of Remsen and Iles[1] by oxidizing the amide



with a mixture of potassium bichromate and sulphuric acid. The acid was purified through the barium salt. This was treated with boiling absolute alcohol to remove unoxidized amide. The acid which crystallized out on cooling was washed until the filtrate gave no reaction for chlorine, and was finally recrystallized from water. It then appeared in the form of thick, lustrous, colorless needles.

According to Remsen and Iles[2] the acid melts at 254°.5–255° (corrected). I found that the melting point can be made to vary considerably according to the rate of heating. In the following all the temperatures given have been corrected:

Manner of heating	Observed melting point
I. Heated rapidly from 20°	247°.7–253°.7
This was cooled to 207°.9 and reheated	244°.6–245°.6
Cooled rapidly in the air and replaced in the hot acid at 232°.1	239°.1–240°.1
On cooling this portion solidified to a clear, brown mass whose melting point could not be determined.	
II. Heated to 245° for eight minutes	245°
On cooling, it formed a clear, light brown mass easily dissolving in water. The solution was very acid and had a nitrile odor.	
III. Heated to 220°.9 for two hours and three-quarters it was completely changed to a clear, brown liquid	220°.9
IV. Heated to 215°.9 for three hours and ten minutes it fused to a clear, brown liquid.	215°.9

[1] THIS JOURNAL, 1, 37.
[2] *Ibid.*, 1, 44 (1879).

V. Heated to 210°.9 for four hours and a quarter there was no apparent decomposition, but it was slightly soluble in water and had a slightly acid reaction..... 210°.9

VI. Heated to 205°.8 for seven hours it was apparently unchanged. It was still insoluble and gave no reaction with litmus.

It will be seen from the above that the lowest temperature at which decomposition takes place is in the neighborhood of 210°. In the course of this investigation, however, the temperature to which the acid was heated was 220°.

In order to determine whether there was any loss in weight on heating the acid, I heated 1.1404 grams to 215° for three hours. It was found to have lost 0.0013 gram = 0.11 per cent.

Preparation and Treatment of the Melt

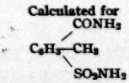
The sulphamidotoluic acid was heated in portions of 25 grams in a small porcelain dish covered with a perforated watch crystal through which a thermometer was thrust directly into the acid. A cylindrical air bath covered with asbestos and provided with a thermostat was used. The acid was heated for a period of five to seven hours to 220°. Before cooling, the thermometer was removed and the dish was placed in a desiccator on account of the deliquescence of the melt. As thus obtained, the melt was a clear, dark brown, brittle mass, deliquescent, very acid, and having an odor of nitriles. Occasionally there were small, irregular crystals throughout the mass, especially if it had stood for a few days. The melt was insoluble in benzene, ligroin, ether and chloroform, but soluble in absolute alcohol, and easily soluble in ordinary alcohol, acetone and water, except one constituent, the "diamide."

The method of treatment adopted was as follows: The melt was treated with three or four times its weight of water and warmed for some time on the water bath. The next morning the fine crystals of the "diamide" were filtered off. When the melt was treated with cold water the "diamide"

appeared in very fine particles that gave the solution a peculiar silky appearance and were very difficult to filter off. The clear filtrate from these would continue to deposit more of them for several days. In either case the filtrate yielded a small second crop of "diamide" on being evaporated to a smaller volume. After this the filtrate was evaporated to dryness and treated with anhydrous acetone. A powdery mass consisting of a little "diamide" with a considerable quantity of acid ammonium *p*-sulpho-*m*-toluate remained undissolved. The clear filtrate was allowed to evaporate spontaneously in a wide dish. This was found to contain free sulphotoluic acid, its acid ammonium salt in small quantity and sulphuric acid.

The "Diamide" and its Derivatives

As already stated, this substance remains nearly all undissolved when the melt is treated with water, alcohol or acetone. To purify it, it was dissolved in quite dilute sodium hydroxide solution, stirred up with a little purified animal charcoal for a few minutes, filtered with the aid of a pump, and then through a double thick paper to remove the considerable amount of fine charcoal that was not held back at first. The filtrate was at once acidified with a slight excess of hydrochloric acid, when the "diamide" was precipitated in crystalline flakes. After standing overnight it was filtered, washed and dried. It resembled in all respects the "diamide" of Muckenfuss and Stoddard. The sulphur and nitrogen in it were determined.



		Found	
S	14.95	15.04	15.03
N	13.09	13.12	13.13

The sulphur, as in all succeeding analyses, was determined by Liebig's method. The nitrogen was determined by the Kjeldahl method, pure sulphuric acid alone being used.

The compound is practically insoluble in boiling water and alcohol and the ordinary organic solvents. It dissolves in

concentrated hydrochloric and nitric acids, but is reprecipitated on diluting. From its solution in concentrated ammonia it is precipitated by acidifying with hydrochloric acid. Its solution in concentrated sulphuric acid may be heated to 200° without apparent decomposition. On diluting with water the compound appears in needles. When dissolved in very dilute sodium hydroxide and then precipitated by dilute hydrochloric acid, it forms, on long standing, beautifully regular crystalline plates, belonging apparently to the orthorhombic system. Under the microscope with crossed Nicols they show interference colors. Frequently their only faces are the prism and the basal plane, so that they appear as thin, diamond-shaped plates with angles approximately equal to 72° and 108°. At times the brachypinacoid occurs. The plates are then irregular hexagons in outline. The needles above mentioned are simply the hexagons elongated in the direction of the brachydiagonal.

The compound is quite soluble in solutions of acid ammonium sulphotoluate. When a rather concentrated solution of the ammonium salt is boiled with some "diamide" and the solution cooled and filtered, a considerable deposit of "diamide" is formed after standing several hours.

Saponification by Alkali.[1]—The "diamide" is readily decomposed by cold, dilute sodium hydroxide. All the nitrogen is driven off as ammonia.

0.2593 gram "diamide" was boiled with sodium hydroxide, the ammonia given off being caught in a measured volume of standard acid.

	Calculated for $C_6H_3(CONH_2)(CH_3)(SO_2NH_2)$ Gram	Found Gram
NH_3	0.04122	0.04113

Saponification by Acid.[2]—Somewhat less than a gram of "diamide" was heated to 200° in a sealed tube with hydrochloric acid for six hours. When the tube cooled a large

[1] THIS JOURNAL, **18**, 355 (1896).
[2] *Ibid.*, **18**, 355 (1896).

part of the "diamide" separated out unchanged. The filtrate was evaporated to dryness on the water bath, and the residue treated with cold water. A little remained behind. The filtrate was evaporated to dryness and extracted with absolute alcohol. The salt crystallizing out from this solution very closely resembled ammonium chloride, with which it must have been somewhat mixed. It was boiled with barium hydroxide, the excess removed by means of carbon dioxide and the filtrate evaporated to crystallization, when the characteristic crystals of barium sulphotoluate appeared.

Saponification by Barium Hydroxide.—Some of the compound was boiled with barium hydroxide. At the end of three or four hours it was found that practically all the nitrogen had been driven off as ammonia:

	Calculated for $C_6H_3(CONH_2)(CH_3)(SO_2NH_2)$ Per cent.	Found Per cent.
N	13.09	12.79

The excess of barium hydroxide was removed by means of carbon dioxide and the filtrate was boiled, filtered and evaporated to crystallization. A typical mixture of the two forms of barium sulphotoluate crystallized out. The determinations of barium and water did not agree for any formula, but were fairly satisfactory for a mixture such as

$$C_6H_3(COO)(CH_3)(SO_3)Ba.H_2O + 3C_6H_3(COO)(CH_3)(SO_3)Ba.2H_2O$$

as will be seen.

	Calculated for mixture containing $1^1/_3$ H_2O	Found I	II	III
Ba	35.86	35.34	35.19	35.80
H_2O	8.11	7.94	7.75	7.75

Magnesium Salt.—In attempting to drive off half of the nitrogen from his "diamide," Stoddard[1] boiled it with magnes-

[1] THIS JOURNAL, 47, 1.

ium hydroxide, and found that the desired result was attained. More recently, Chamberlain[1] found that somewhat more than half of the nitrogen was driven off by boiling a couple of days. The same is true of the compound here under investigation.

The filtrate from the excess of magnesium hydroxide in these experiments gave a crystalline powder on evaporation to a small volume. On boiling with sodium hydroxide it gave off ammonia, showing that it was probably similar to the salt $\left(C_6H_4\begin{matrix}CONH_2\\SO_3\end{matrix}\right)_2Mg.4H_2O$ obtained by Stoddard. Accordingly larger quantities of it were made as before. The salt was never obtained in good crystals, but always in a finely granular form not easy to dry for analysis. The water of crystallization was determined in a sample dried by standing overnight on a porous plate:

	Calculated for $\left(C_6H_3\begin{matrix}CONH_2\\CH_3\\SO_3\end{matrix}\right)_2Mg.4H_2O$	Found		
H_2O	13.74	13.32	13.46	13.62

Magnesium and nitrogen were determined in a specimen dried at 150°.

	Calculated for $\left(C_6H_3\begin{matrix}CONH_2\\CH_3\\SO_3\end{matrix}\right)_2Mg$	Found	
Mg	5.31	5.27	5.27
N	6.19	6.06	5.96

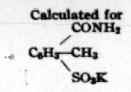
The magnesium was determined as pyrophosphate in the usual manner.

Potassium Salt.—This was obtained in the form of a fine crystalline powder. The water was determined in a specimen dried on a porous plate:

	Calculated for $C_6H_3\begin{matrix}CONH_2\\CH_3\\SO_3K\end{matrix}.H_2O$	Found	
H_2O	6.64	7.14	7.24

[1] See p. 326.

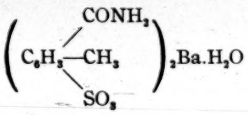
Some of the salt dried at 140° was used to determine nitrogen and potassium:

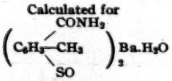


	Calculated for $C_6H_3(CONH_2)(CH_3)(SO_2K)$	Found	
K	15.41	15.71	15.75
N	5.53	5.18	5.24

The potassium was weighed as sulphate.

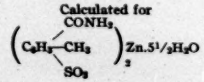
Barium Salt.—This was prepared by precipitating the magnesium from a solution of the magnesium salt by means of a slight excess of cold, dilute barium hydroxide. The excess of barium was removed by passing carbon dioxide into the filtrate and then boiling. The filtrate yielded, on evaporating to a small volume, a salt in very short, fine needles. By analysis it was found to be



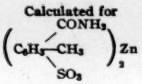


	Calculated for $[C_6H_3(CONH_2)(CH_3)(SO)]_2Ba.H_2O$	Found	
Ba	23.50	23.22	23.63
N	4.80	4.67	4.71
H_2O	3.09	3.62	3.78

Zinc Salt.—This was made by precipitating the barium from the preceding salt by means of zinc sulphate. The easily soluble salt formed fine, short needles:

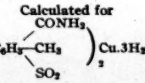


	Calculated for $[C_6H_3(CONH_2)(CH_3)(SO_3)]_2Zn.5\frac{1}{2}H_2O$	Found	
H_2O	16.72	16.83	17.28



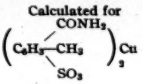
	Calculated for	Found		
Zn	13.18	14.22	13.93	13.54
S	12.96	12.05	12.82	
N	5.68	5.07	5.13	

Copper Salt.—This was made in the same way as the zinc salt. On evaporating the filtrate from the barium sulphate to a small volume a powdery salt of a light blue color was obtained. The analyses were unsatisfactory:



	Calculated for	Calculated for $4H_2O$	Found	
H_2O	9.91	12.78	10.75	11.38

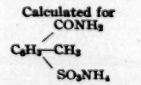
The salt began to turn brown at about 200°. A specimen dried at 170° was analyzed.



	Calculated for	Found			
Cu	12.83	12.22			
N	5.70	5.34	4.58	4.53	4.34

Ammonium Salt.—On adding ammonium sulphate to the barium salt and evaporating the filtrate to crystallization, a most satisfactory ammonium salt was obtained. Although very soluble in water, it readily formed good crystals from very concentrated solutions. The crystals were rectangular prisms containing no water of crystallization.

0.2343 gram lost 0.0002 gram on heating to 175°.



	Calculated for	Found	
S	13.79	14.18	
N	12.07	11.57	12.14

Microscopical Examination of the Melt

In order, if possible, to learn something about the formation of the "diamide" from the perfectly transparent melt when

treated with solvents, the microscope was used. A thin, clear fragment of the melt was at first perfectly dry, but it soon began to attract moisture from the air, and at the same time slender, needle-shaped crystals appeared on the surface, radiating from a center or crossing one another at all angles. Peculiar Y-shaped crystals were frequently seen. On longer exposure to the air curious irregular scales seemed to grow out on the needles, and later the whole surface of the melt was covered with these scales arranged in rosettelike groups. In many fragments of the melt there appeared imbedded in the glassy mass groups of very irregular crystals, appearing as groups of plates with serrate edges or as octahedra with very uneven faces. All attempts to keep sight of these on dissolving the melt failed on account of the great number of scales which filled the field.

A small fragment of the melt was fused on a slide and covered with a thin glass which was pressed down so as to make a thin layer of the melt. On long standing in the air, when cooled, the edges of the melt began to attract moisture, and fine needles shot in under the cover glass. On placing a drop of water at the edge the needles dissolved at once, and at the same time curious rosette-shaped masses of "diamide" appeared in great numbers. Another experiment of this sort was more interesting. Only a very small fragment of the melt was fused on the slide, so that it did not spread out to the edges of the cover glass. A drop of water was then run in under the edge of the cover. At once large numbers of "diamide" flakes seemed to spring into existence near the edge of the melt and floated away in the water, increasing in size up to a certain limit. When the water became saturated, fine needles began to form in an irregular zone close to the unattacked part of the melt, but separated from it by a sharply defined clear zone of solution. Passing outward from the melt the needles became fewer and fewer, and were mixed with small "diamide" masses that became larger and larger as the needles disappeared and the solution became more dilute. After standing overnight in a moist chamber, it was found that the irregular masses of "diamide" had wholly, or in part, changed over

into the usual crystalline particles. Judging from the various shapes of the particles it seemed that the rosettes had broken up in part and acquired their geometrical form one side at a time. There were pieces with one, two or more straight edges, the rest of the outline being an irregular curve. With acetone similar phenomena were seen.

It appears from the above that the presence of water, or of some other solvent, is necessary for the formation of the "diamide" in its ordinary condition. It is, no doubt, a case of solid solution in which the "diamide" is dissolved by acid ammonium sulphotoluate. Water dissolves this with the greatest ease, forming a solution which can dissolve the "diamide" to a certain extent, as we have seen. From such a solution the "diamide" can be precipitated by diluting. The gradual transformation of amorphous precipitates into the crystalline form on standing in the solution from which they were thrown down is well known, so that we have at hand what appears to be an explanation of all the phenomena noticed on treating the melt with water. At first the excess of "diamide" separates out. The needles appear when the solution begins to be supersaturated. But farther out from the melt, the solution is more dilute, the needles are fewer and the "diamide" begins to separate out again. Finally, on long standing, the "diamide" becomes crystalline.

p-*Sulpho*-m-*toluic Acid*

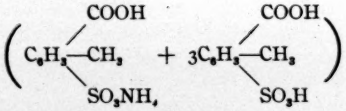
This acid was not obtained in pure condition, but a number of its salts were made and will be described later. Apparently this particular sulphotoluic acid had never been made before, no reference to it being found in the literature.

A small quantity of the impure acid was obtained from the portion of the melt soluble in acetone. When this evaporated spontaneously, a thin, dark brown crust of fine needles mixed with a moist, tarry substance was formed. It was dissolved in water and boiled with animal charcoal, filtered and evaporated to a small volume. The first lot of crystals consisted mainly of the acid ammonium salt. The mother liquor on further evaporation became very syrupy and yielded a small

quantity of crystals. They were dried on a porous plate and analyzed. The small percentage of nitrogen found must have been due to an admixture of the ammonium salt.

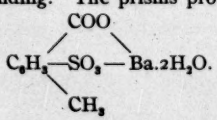
	Calculated for	Found	
S	14.81	12.96	
N	0.0	1.57	1.62

Not enough was obtained for satisfactory analyses. A mixture of the composition



contains about 1.5 per cent. of nitrogen.

Barium Sulphotoluate.—Failing at first to obtain any satisfactory products from the alcoholic or water extracts of the melt after removing the "diamide," these solutions were boiled with an excess of barium hydroxide until all the ammonia was driven off. A small quantity of barium sulphate mixed with some organic matter remained undissolved. The excess of barium hydroxide was removed by precipitating with carbon dioxide, boiling and filtering off the barium carbonate. The filtrate was evaporated to crystallization. It did not readily yield good crystals on long standing, or on evaporating on the water bath. Usually the salt came down in a powdery mass of very fine needles, or as a mixture of these with prisms. But from one solution very good crystals were obtained in the form of prisms with one or two sides curved. Both forms were found to be barium sulphotoluate, but with different amounts of water of crystallization. A solution of the prisms yielded needles when evaporated on the water bath and cooled. A solution of the needles yielded a mixture of needles and prisms on long standing. The prisms proved to be the salt



	Calculated for $CH_3C_6H_3\langle^{COO}_{SO_3}\rangle Ba.2H_2O$	Found		
Ba	35.40	35.30	35.24	35.32
H_2O	9.30	9.21	9.36	

The purest sample of needles obtainable was analyzed for water of crystallization:

	Calculated for $CH_3C_6H_3\langle^{COO}_{SO_3}\rangle Ba.H_2O$	Found
H_2O	4.88	5.77

There was probably a slight admixture of the other salt.

Acid Barium Sulphotoluate.—A solution of barium sulphotoluate was divided into two equal portions and the barium was exactly precipitated from one-half by means of sulphuric acid. The filtrate from the barium sulphate was added to the second half and the whole evaporated to a small volume. The acid salt formed small round masses consisting of fine needles. It was shown by analysis to have the composition

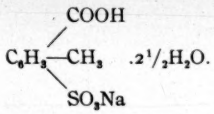
$$\left(C_6H_3\langle^{COOH}_{CH_3}\rangle SO_3\right)_2 Ba.5H_2O.$$

It was efflorescent.

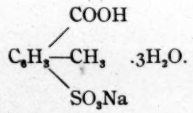
	Calculated for $\left(C_6H_3\langle^{COOH}_{CH_3}\rangle SO_3\right)_2 Ba.5H_2O$	Found	
Ba	20.85	20.90	20.61
H_2O	13.70	13.27	

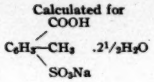
Acid Sodium Sulphotoluate.—In purifying the "diamide," which still retained a considerable quantity of the extract of the melt, it was dissolved in sodium hydroxide. This not only hydrolyzed some of the "diamide," but also drove out the ammonia from the acid ammonium sulphotoluate which was present. When the "diamide" was precipitated by means of hydrochloric acid, acid sodium sulphotoluate was formed. The latter was obtained by boiling down the

filtrate from the "diamide." It was much less soluble than the sodium chloride. When obtained by cooling a concentrated solution the salt appeared in fine needles of the composition

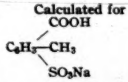


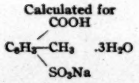
On redissolving and evaporating rather slowly the salt formed irregular hexagonal plates of the composition



	Calculated for 	Found	
H_2O	15.90	15.78	16.32
Na	8.13	8.85	

In the salt dried at 140°:

	Calculated for 	Found
Na	9.66	9.43

	Calculated for 	Found
H_2O	18.49	18.59

Unless exactly the right conditions were hit upon, the saturated solution of the salt deposited crystals very slowly. Such a solution, in which had been placed a fragment of a crystal, stood for a week or more over sulphuric acid without apparent change.

Acid Ammonium Sulphotoluate.—This salt was obtained by

several different methods, but it always formed very slender, extremely soluble, anhydrous needles that were stable in the air. On heating gently on platinum foil it fused, blackened, and gave off sulphur dioxide and a substance having a strong nitrile odor. The salt was easily prepared from the melt as follows:

The water extract of the melt was evaporated to dryness on the water bath and the powdered residue shaken up with anhydrous acetone and allowed to stand some hours. A brown powder, very soluble in water and with a strong acid reaction, was left undissolved. It was washed with acetone, dissolved in water and boiled with animal charcoal, and the solution filtered and evaporated to a small volume. Usually a little "diamide" would crystallize out. The filtrate from this contained very little "diamide." It was then evaporated to a smaller volume and cooled. Often almost the entire contents of the beaker would solidify to a mass of very fine, long needles, so that the beaker could be inverted without spilling anything, yet, on warming to the temperature of the hand, everything would go into solution again. The crystals would at times shoot out in all directions from a single point on the bottom of the beaker to the sides. If the solution was evaporated too far and cooled, the salt would appear in very fine particles resembling the "diamide" very closely, but easily distinguishable from it by their great solubility. The salt was filtered off and dried on a porous plate. It formed a nearly pure white powder that was not deliquescent.

	Calculated for $C_6H_3(COOH)(CH_3)(SO_2NH_4)$	Found		
S	13.73	12.95	13.43	13.67
N	6.01		5.66	

0.3330 gram heated to 170° lost 0.0023 gram.

In order to be sure that the pasty mass resembling the "diamide" was really acid ammonium sulphotoluate some of it was dried on a porous plate and analyzed. Part of it was

recrystallized and from it the characteristic needles were obtained.

	Calculated for $C_6H_3(COOH)(CH_3)(SO_3NH_4)$	Found
S	13.73	13.90
N	6.01	6.09

On one occasion the portion soluble in acetone yielded small rounded crystalline masses that were nearly insoluble in anhydrous acetone. These proved to be the acid ammonium salt mixed with some free acid.

	Calculated for $C_6H_3(COOH)(CH_3)(SO_3NH_4)$	Calculated for $C_6H_3(COOH)(CH_3)(SO_3H)$	Found	
S	13.73	14.82	14.61	
N	6.01	0.0	4.19	4.39

When the acid ammonium sulphotoluate was prepared from the barium salt, it appeared in fine needles. These were shorter, thicker and much less soluble than those obtained from the melt. They also had a decided tendency to crystallize in roundish masses instead of uniformly throughout the solution. This was so marked that in two or three instances, when the solution was about 5 mm. deep in the beaker, the salt in crystallizing drew together in irregular masses so that the bottom of the beaker was uncovered in spots. When the salt obtained from the melt crystallized, the surface of the mass was usually smooth. The salt was analyzed:

	Calculated for $C_6H_3(COOH)(CH_3)(SO_3NH_4)$	Found
S	13.73	14.09
N	6.01	5.94

0.3721 gram when heated to 175° lost 0.0007 gram.

It had, therefore, the same composition as that from the melt. The difference between the two salts cannot be accounted for at present.

The barium was exactly precipitated from a solution of the sulphotoluate by means of ammonium sulphate. On evaporating to a small volume the solution of ammonium salt thus obtained, crystals exactly resembling the acid ammonium salt just described were obtained. Analysis showed that the two were identical:

	Calculated for $C_6H_3(CONH_4)(CH_3)(SO_3NH_4)$	Calculated for $C_6H_3(COOH)(CH_3)(SO_3NH_4)$	Found
S	12.80	13.73	13.59
N	11.20	6.01	5.68

This result could be due only to a loss of ammonia on evaporating the solution. The salt had a strong acid reaction, and when treated with a little dilute ammonia there was a marked evolution of heat. A solution containing 0.7212 gram of the salt was neutralized with dilute ammonia, requiring 10.17 cc. It was then heated a couple of hours on the water bath, when it required 2.1 cc. for neutralization. It was then evaporated to dryness, redissolved, again evaporated to dryness, and finally redissolved. It then required 2.0 cc. of ammonia for neutralization.

Preparation from p-*Sulphamido*-m-*toluic Acid*.—Some of the sulphamidotoluic acid was heated with concentrated hydrochloric acid in a sealed tube to 200° for several hours. The solution was evaporated to dryness, the residue dissolved in water and crystallized. It formed needles in groups like those from the barium salt.

	Calculated for $C_6H_3(COOH)(CH_3)(SO_3NH_4)$	Found
S	13.73	13.84
N	6.01	5.64

m-*Tolunitrile*

In determining the melting point of the sulphamidotoluic acid it was noticed that whenever it had been heated long enough to turn brown, the odor of nitriles was observed

on crushing the capillary tube. In order to obtain some of this substance for identification, some of the melt was placed in a test tube which was then drawn out so as to form a miniature retort. On heating in acid potassium sulphate to 295° the melt began to foam up and give off sulphur dioxide. On heating higher with a free flame, an acid liquid mixed with oily drops distilled over. On cooling, the oil solidified into white, crystalline flakes. The liquid was probably water in which was dissolved some sulphur dioxide. The entire distillate was put into a sealed tube with dilute hydrochloric acid and heated in a water bath for an hour. On cooling, white needles and a yellowish oily globule were seen. Even when heated to 130° for several hours with stronger acid there was no decrease in the size of the globule, and the contents of the tube still had the odor of nitriles. The needles melted at 96°–112°.3 and the globule at 91°–112°. The entire solid product was treated with a dilute solution of sodium carbonate, which dissolved everything but a little nitrile. On acidifying the solution a dense white precipitate was thrown down. It was found to melt at 110°.75 (corr.). At about 93° a very small portion on the walls of the capillary began to melt, and even when kept at 110°.75 it took about a minute for all the acid to melt. Even after the acid had been distilled with steam there was no change in its behavior. It melted under boiling water. It was in all probability metatoluic acid. Not enough for analysis was obtained. The nitrile was no doubt *m*-tolunitrile.

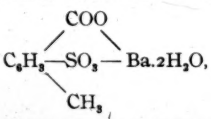
Discussion of Results

From a consideration of the facts set forth in this article, it may be concluded that, in the main, *p*-sulphamido-*m*-toluic acid and *p*-sulphamidobenzoic acid undergo similar transformations when heated. Each yields an insoluble, infusible substance having the empirical composition of the diamide of the sulpho acid. From these, both nitrogen atoms are driven off as ammonia by sodium hydroxide, which shows that no sulphamido grouping is present; for sulphamido acids are scarcely, if at all, attacked by boiling with strong sodium

hydroxide solution. Further, the two nitrogen atoms must be differently arranged in the "diamides," for only one is driven off by boiling with magnesium hydroxide. From the magnesium salts thus obtained the remaining nitrogen is driven off as ammonia by sodium hydroxide. That the magnesium salt is derived from a new acid isomeric with the sulphamido acid is most clearly shown by its forming an ammonium salt in well-defined prisms entirely unlike the sulphamidotoluate of ammonium, which forms fine needles. Besides, the free acid is easily soluble in cold water, the sulphamido acid being nearly insoluble. Further investigation along this line is evidently necessary. The carbamidosulphonic acid should be made for comparison.

In both investigations the main product obtained was the acid ammonium salt of the sulpho acid. We found that the acid ammonium sulphotoluate from the melt was not identical with the salt made by saponifying the sulphamido acid. That obtained from the barium sulphotoluate was identical with the latter.

In each investigation some free sulpho acid was found to be present. Its formation seems to be necessary in order to furnish the second nitrogen atom to the "diamide." The sulphotoluic acid yielded but one well-characterized salt,



the other salts made being obtained in fine needles of no characteristic appearance.

In working with the melt of the sulphamidotoluic acid, no evidence to show the existence of an acid analogous to the "iso" acid of Muckenfuss[1] and of Stoddard[2] was obtained, except that the alcoholic extract of the melt deposited on cooling a small quantity of some flocculent substance.

JOHNS HOPKINS UNIVERSITY

[1] THIS JOURNAL, **18**, 361 (1896).
[2] *Ibid.*, **17**, 1.

REVIEWS

Mischen, Rühren, Kneten und die dazu verwendeten Maschinen. Von Dr. Ing. Hermann Fischer, Geh. Regierungsrat und Professor. Mit 122 Figuren im Text. (Chemische Technologie in Einzeldarstellungen. Herausgegeber, Prof. Dr. Ferd. Fischer, Göttingen.) Leipzig: Verlag von Otto Spamer. 1911. S. 90. Preis: geh., M. 5.75; geb., M. 7.00.

The aim of the author has been to discuss the principles of the operations of mixing, stirring and kneading as carried out in industrial chemical work, and to describe by diagrammatic sketches some of the leading forms of apparatus used, as far as this is necessary to show some applications of the principles.

The object of mixing substances is discussed in a general introductory chapter; examples of mixing solids, liquids and pasty substances give an idea of the wide scope of the operations. The different methods of dealing with dry and pasty material are outlined, e. g., bedding, followed by cutting in the case of dry, and by folding with pasty, substances; mixing dry materials by raking and shoveling, spreading and heaping; and mixing pasty materials by various mechanical devices. Intermittent and continuous work are considered as well as the examination of a prepared mixture as to its uniformity.

In the second part, intermittent work, that is, the mixing of liquid charges, of thick and thin pastes, and of pulverulent materials, is outlined. With liquids there is given some space to compressed air which in recent years usually replaces the former hand stirring; different mechanical devices are noted, from the egg beater to various mechanical stirrers in large, stationary vessels. Turning to pasty substances, the apparatus for liquid pastes resembles that used for liquids, while with stiff pastes the field of kneading machines becomes prominent. In the mixing of dry materials, different forms of drums, mooth and corrugated, bucket elevators, Archimedean screws, and sifting apparatus receive due consideration.

Continuous mixing, which forms Part III, is shown to require a uniform feeding of constituents if a product of unchanging composition is to be obtained. The constituents either form separate steady streams of definite cross sections and speed, or they follow one another in predetermined quantities in a given succession. Continuous feeding of gases and liquids is difficult on account of irregularities in flow due to variations in pressure; with liquids alone the result is more even, and very simple mechanical devices give good results;

pasty materials are kneaded with plane rolls, screw propellers working in vertical cylinders, or horizontal troughs: the general principle followed with solid substances is to discharge the content of a hopper by mechanical feeders of the oscillating, slowly reciprocating, bumping, scraping, or rolling types.

Mixing of the uniformly fed constituents finally is accomplished in various ways. The principles that govern the designs of apparatus are mostly the same as with the intermittent devices, excepting, of course, that the feed and discharge are continuous.

The subject covered in this book of 84 octavo pages is very broad, too broad, it seems, to be compressed into such a small space. Accepting the limits the author set himself, the book leaves the reader unsatisfied, as he had a right to expect more and did not receive it. He is reminded of an amplified table of contents of a larger book which deals quantitatively with the subject, while he has received only qualitative treatment, which is very attenuated at that. H. O. HOFMAN.

SULFURIEREN, ALKALISCHMELZE DER SULFOSÄUREN, ESTERIFIZIEREN. Von. DR. A. WICKELHAUS, Geheimer Geg.-Rat., Professor an der Universität Berlin. Mit 32 Figuren im Text und 1 Tafel. (Chemische Technologie in Einzeldarstellungen. Herausgegeber, PROF. DR. FERDINAND FISCHER.) Göttingen: Verlag von Otto Spamer. 1911. S. vi + 130: Preis: geh., M. 7.50; geb., M. 8.75.

Like the other books of this series, the present volume is attractive and readable. The theoretical and practical portions are well balanced, and the illustrations distinc and well chosen. The grouping of topics is somewhat unusual. The central idea seems to be the use of sulphuric acid, and about this are grouped a number of technical operations which in ordinary practice depend upon the use of that reagent. Closely allied operations are often included.

The topics especially discussed are: the preparation of Turkey-red oil; the acid hydrolysis of the fats; the preparation of sulphonic acids; the preparation of phenols from sulphonic acids; and esterification. In the treatment of the latter subject, the author seems to be in doubt as to whether certain topics really belong to him or whether they are to be treated more fully in some other volume of the series. This makes the treatment half-hearted, and the reader is left in doubt as to where more detailed information should be sought.

The book is interesting and suggestive throughout, but in its later portions the reader misses sufficient references to the literature to enable him to look up the details of many of the topics mentioned. This is an unusual lack in a German

book, and the criticism does not apply to the earlier pages, which seem to have received more careful treatment.

F. J. Moore.

THE MANUFACTURE OF SULPHURIC ACID AND ALKALI, with the Collateral Branches. A Theoretical and Practical Treatise. By GEORGE LUNGE, PH.D., Professor Emeritus of Technical Chemistry in the Federal Polytechnicum, Zurich. Third Edition. Volume III. Ammonia-Soda, Various Processes of Alkali Making and the Chlorine Industry. New York: D. Van Nostrand & Co. 1911. pp. xix + 764. Price, $10.00.

This well known work by Professor Lunge has long stood as an authoritative treatise upon the industries with which it deals, and here in the new and enlarged third edition is brought together the latest information which has appeared in scientific or technical literature up to about 1909. To those readers already acquainted with the earlier editions, it will be at once apparent that the author still retains his vigorous style; to a critical study of the published papers he frequently adds positive expressions of his own personal views concerning the topics in question. It is the author's aim to offer to the reader a complete survey of the whole field, so there are included many antiquated and impractical processes, which nevertheless have occasional interest to the specialist. Details of processes are especially studied and inherent defects or obstacles to successful technical application are brought out.

The first nine chapters, comprising 212 pages, are devoted to the Ammonia-Soda Process. Opening with a history of the process, the author next passes to a discussion of the theory as presented by different writers, especially from the physical-chemical point of view. But in summing up the results of many investigations, the opinion is expressed that as yet the practical manufacturer has received but little real advantage from the purely scientific studies that have been made of the process, owing to the wide difference of conditions in the two cases; but the author hopes for more success in the future, through better coöperation between theory and practice.

The remarks upon the materials necessary, the expense factors of the process, and the advantages and disadvantages as compared with the LeBlanc process, are very interesting reading. Improvements recently introduced into the process, especially in connection with the production of lime and recovery of carbon dioxide and the testing of the gases, are outlined. Statistics have been revised and certain recent proposals for making ammonia-soda are noted; thus, the Frasch nickel oxide ammonia-soda process, and Haas' borax process with recovery of hydrochloric acid. Chapters X to

XIV, inclusive, pp. 213 to 324, are devoted to processes, other than the LeBlanc, proposed for making soda. Aside from the old Cryolite Process here described in detail, none of these methods appears to be in technical use at present. Chapters XV to XXIII, pp. 325 to 736, deal with the Chlorine Industries which are based on "purely chemical" processes; the electrolytic manufacture of chlorine and alkali is consigned to Vol. IV, to appear shortly. A readable and up-to-date history of the chlorine industries opens this third part of the book, followed by a discussion of the properties of gaseous and liquid chlorine, and including an account of its physiological action. The Weldon and Deacon processes are considered in detail and in the case of the latter process we find recent proposed improvements, such as the use of pure oxygen instead of air; contact mass containing certain rare-earth chlorides; and the use of double salts to reduce the volatility of the cupric chloride. An excellent résumé of articles on the constitution of bleaching powder and of bleach liquors includes the recent investigations of Winteler, Foerster, Tarugi, Ditz and others, with comments by the author. Among the descriptions of technical manufacture, we find reference to the new process of the Griesheim-Elektron Co., for crystalline calcium hypochlorite, and a discussion of the properties of the substance. Concerning the making of bleach solutions and the use of certain proprietary preparations, the author's investigations have caused him to form very positive opinions in many cases. The final chapter of the book, dealing with chlorates and their preparation by the old Liebig process, is chiefly of historical interest now; the newer electrolytic methods have been reserved for Vol. IV.

Through the book are scattered about 184 illustrations of apparatus, nearly all of which appeared in the earlier editions, but an occasional new figure is found, as Fig. XVIII, an improved type of lime-kiln to include recovery of the carbon dioxide. Statistics of the manufacture of alkali and chlorine products constitute the Appendix. The book will be most useful to technical men having to deal with heavy chemical manufacture, and as a reference book should be placed in all libraries.

F. H. Thorp.

Lubricating Oils, Fats and Greases. Their Origin, Preparation, Properties, Uses and Analysis. By George H. Hurst, F.C.S., Late Lecturer on Oils at the Municipal Technical School, Manchester. Third Edition, Revised and Enlarged, by Henry Leask. With Seventy-four Illustrations. London: Scott, Greenwood & Son; New York: D. Van Nostrand & Co. 1911. pp. xv + 390. Price, $4.00.

The original text has been altered but slightly, the chief

changes being in Chapter VIII on Lubrication, reprinted from an article by J. V. Wilson in the *Journal of the Institute of Marine Engineers;* the appendix contains several chapters reprinted from the "Oil and Colour Trades' Journal" upon the lubrication of internal explosion engines, motor greases, recipes and patents.

Owing to the fact that practically no alterations have been made in the original text for ten years, this book can hardly be recommended either technologically or analytically. A noticeable feature of the volume is the paucity of reference to original articles which could well have been included. On the other hand, the chapters upon Lubrication are excellent; the recipes will no doubt be found useful, and are features which really make the book worth having. A. H. GILL.

THE MANUFACTURE OF CHEMICAL MANURES. By J. FRITSCH. Translated from the French, with Numerous Notes, by DONALD GRANT. With Sixty-nine Illustrations and One Hundred and Eight Tables. London: Scott, Greenwood & Co.; New York: D. Van Nostrand & Co. 1911. pp. xvi + 339. Price, $4.00.

This is a translation of a French author, who states that his technical information has been secured largely from German sources. It deals fully with the composition and sources of phosphates, potash salts and nitrogenous manures, the manufacture of superphosphates, double superphosphates, bone dust, basic slag, ammonia salts, cyanamide, fish guano, etc. It discusses the history, theory and methods of manufacture of phosphatic and other fertilizers, with 69 cuts of plans of machinery and apparatus. This book is excellent for one who desires a treatise on the chemistry and principles of the manufacture of fertilizers, or who wishes to become familiar with European methods. American manufacture is somewhat different, but our manufacturers can no doubt secure helpful information by studying the methods of their European competitors. G. S. F.

GALVANOSTEGIE. I. TEIL. Über elektrolytische Metallniederschläge. Von DR. ING. M. SCHLÖTTER. Mit 22 Figuren im Text. Monographien über angewandte Elektrochemie. XXXVII. Band. Halle a. S.: Verlag von Wilhelm Knapp. 1910. pp. xiv + 257. Price, M. 12.00.

This book seems to be the first attempt to give a scientific treatment of the subject of electrometal deposition and is therefore a publication of unusual interest.

Electroplating is probably the oldest industry in the subject of Applied Electrochemistry, for the reason that it could be applied even before the advent of dynamo-electrical machinery, and perhaps because it had this early start we find

the whole subject lacking in scientific treatment. Rule-of-thumb methods were used in the beginning, and have continued almost down to the present time.

Recently, however, attention has been directed to the subject by electrochemists and a great deal of information is now available on the deposition of metals electrolytically.

The present book has brought together this information in the form of a volume which is one of the excellent series of monographs dealing with the subject of applied electrochemistry.

The aim has been to take up the subject by giving the results of researches which have been conducted for any particular metal and it is surprising to find what a large literature there is, many of the references being to patents.

Thus we find information on the electrodeposition of copper, silver, nickel, cobalt, iron, gold, zinc, tin, alloys, etc., treated in a way which is quite different from the usual electroplater's handbooks which, for the most part, consist of a long list of receipts for the various baths employed. Particular attention is given to the influential factors, such as current density, temperature, addition reagents, etc., which are taken up in a thorough manner.

The book is well arranged, abundant references are furnished and it is a great contrast to many German books whose authors seem to think they have done all that is necessary when they have given a long list of patents bearing on the subject, without comment or regard to their merits.

Mention should have been made of the very able paper by S. Field on the conditions which determine the compostion of electrodeposited alloys of copper and zinc, which was published in the Transactions of the Faraday Society for 1903.

The volume forms a valuable addition to the subject and should be very helpful to any one engaged in the study of the deposition of metals electrolytically. SAMUEL A. TUCKER.

APPLIED ELECTROCHEMISTRY. By M. DE KAY THOMPSON, Ph.D., Assistant Professor of Electrochemistry in the Massachusetts Institute of Technology. New York: The Macmillan Company. 1911. pp. xii + 329. Price, $2.10.

The subject of applied electrochemistry has now become so large and important that a book in English dealing with this branch of science demands particular attention.

The great difficulty in writing such a book is in the rapid developments which are being made in the subject and it seems as if the method followed in Germany, of issuing monographs on a particular branch of applied electrochemistry,

was really more practical than attempting to include them all in one book.

In the present volume, Professor Thompson has fifteen chapters, ten of which deal with electrolysis in the wet way, the remaining chapters being devoted to the electric furnace and its products. There are necessarily a great many processes to be described in such a program, but notwithstanding this a considerable part of the space is devoted to theoretical considerations. While the theoretical discussion is important, there are many good books which deal with this exclusively, and it would seem better to have expanded the description of the actual processes themselves. Thus the refining of copper, which is an electrochemical process of the first magnitude, is described in seven pages, and aluminium, which is manufactured on a very large scale, is dealt with in five pages, and the actual process is described in a few lines without illustration.

The book as a whole, however, serves a very useful purpose, giving a great deal of information on a long list of subjects. Abundant references are furnished and the illustrations are excellent. One typographical error occurs, however, which seems a pity; the name of Moissan is invariably printed *Moisson*.

The contents of the book is as follows: Coulometers, Electrochemical Analysis, Electroplating, Winning and Refining Metals in Aqueous Solution, Reduction and Oxidation. Electrolysis of the Alkali Chlorides, Electrolysis of Water, Primary Cells, The Lead Storage Battery and the Edison Storage Battery, The Electric Furnace and Products of the Arc and Resistance Furnaces, Electrometallurgy of Iron and Steel, Fixation of Atmospheric Nitrogen, The Production of Ozone, Appendix, Name and Subject Indexes. S. A. T.

CONTRIBUTION À L'HISTOIRE DE LA CHIMIE à propos du livre de M. Ladenburg sur l'histoire du développement de la chimie depuis Lavoisier. Par A. COLSON, Professeur à l'École Polytechnique. Paris: Librairie Scientifique A. Hermann et Fils. 1910. pp. 130. Price, Fr. 3.00.

Ladenburg's book, a French translation of which by Corvisy has recently been published,[1] has been criticized as laying too much stress, especially in the later chapters, on German investigations. Professor Colson points out, however, that this is but natural, especially in view of the splendid facilities at the command of German chemists and the wide publicity given to their publications, as compared with conditions in France.

[1] THIS JOURNAL, **42**, 559.

This contribution to the history of chemistry is in no wise conceived in a spirit of criticism of Ladenburg's book which, all the way through, is spoken of in the highest terms; the author's object has been to call attention to work, chiefly by French chemists, which, in his opinion, has had considerable influence on the development of the science but which is either not mentioned or not sufficiently emphasized in Ladenburg's book. The reviewer, however, must confess to a feeling of disappointment after reading the book, for although its avowed object is undoubtedly fulfilled to some extent, the treatment is so fragmentary and disconnected that no clear impression is left on the reader's mind. The first two chapters deal with the development of the conceptions of the molecule and the atom, of radicals and types and of valence. Gaudin's memoir,[1] in which he so clearly brings out the distinction between the molecule and the atom, deserves special notice. The tetravalence of carbon, the inability to explain certain phenomena on this basis and the author's own views on the application of the tetrahedral formula to stereoisomeric compounds are discussed in the third chapter. The fourth chapter is devoted chiefly to a discussion of catalytic phenomena and to reactions which could not have been predicted theoretically. In the fifth chapter are taken up a number of problems in inorganic chemistry, especially that of complex salts and of the composition of substances in solution. The sixth chapter deals briefly with radioactive phenomena. In the seventh are discussed chemical statics and dynamics; in the eighth, thermochemistry; in the ninth, solid solutions and metallography or "siderology;" and in the last chapter, colloids. C. A. R.

THE IDENTIFICATION OF ORGANIC COMPOUNDS. By G. B. NEAVE, M.A., D.Sc. (St. Andrews), and I. M. HEILBRON, Ph.D. (Leipzig), F. I. C., Lecturers and Demonstrators, Department of Chemistry, Glasgow and West of Scotland Technical College. London: Constable & Co. 1911. pp. viii + 103.

In the preface the authors state their reason for publishing this book: "In teaching practical organic chemistry we have found the want of a convenient text-book dealing with the identification of simple organic compounds, such as is required by students working for the intermediate and final examinations of the institute of chemistry. The scheme adopted in the book has given satisfactory results in the laboratories of the Glasgow and West of Scotland Technical College and the authors now venture to give it wider publicity." In the first section various preliminary tests are given and in Section

[1] Ann. chim. phys., [2] **52**, 113 (1833).

Two tests for the elements liable to be present in organic compounds. Section Three is devoted to group reactions and the remaining sections take up the hydrocarbons and their derivatives in order, giving brief descriptions of their reactions and physical constants.

The book is small and compact and doubtless answers the purpose for which it was printed quite well. W. R. O.

AMERICAN COMMISSION ON ORGANIC NOMENCLATURE

An American Commission of Organic Nomenclature has been appointed, consisting of the following:

Prof. M. T. Bogert, Columbia University, *Chairman*
Pres. Ira Remsen, Johns Hopkins University
Prof. W. A. Noyes, University of Illinois
Prof. T. B. Johnson, Yale University
Prof. M. Gomberg, Univ. of Michigan
Prof. J. F. Norris, Simmons College
Prof. J. B Tingle, McMaster University
Dr. C. H. Hudson, Bur. of Chemistry, U. S. Dept. of Agriculture.

This commission will coöperate with similar national bodies in other countries in the revision of the Nomenclature of Organic Compounds.

Suggestions as to the general plan to be pursued in undertaking this work, or concerning special groups of compounds, will be welcomed, and should be sent direct to the Chairman at Columbia University. MARSTON TAYLOR BOGERT,
Chairman

ERRATUM

P. 230, l. 10, the formula should be

$$\Sigma = \frac{\log \tan \frac{\alpha_1}{2} \log \tan \frac{\alpha_2}{2}}{1/d \text{ (cm.)}} \times 2$$